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THE PRINCIPLES

OF

INORGANIC CHEMISTRY

THE PRINCIPLES

OF

INORGANIC CHEMISTRY

BY

WILHELM OSTWALD

TRANSLATED WITH THE AUTHOR'S SANCTION

BY

ALEX. FINDLAY, M.A., Ph.D., D.Sc.

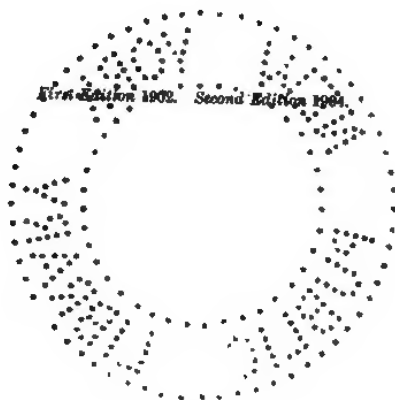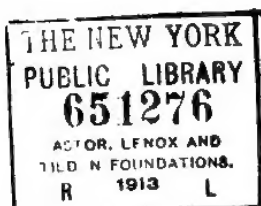LECTURER ON PHYSICAL CHEMISTRY, UNIVERSITY OF BIRMINGHAM

WITH 126 FIGURES IN THE TEXT

SECOND EDITION

London

MACMILLAN AND CO., LIMITED

NEW YORK: THE MACMILLAN COMPANY

1904

First Edition 1902. Second Edition 1904.

DEDICATED

TO MY DEAR WIFE

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IN GRATITUDE FOR LOYAL HELP

TRANSLATOR'S PREFACE
TO SECOND EDITION

In the present English edition the translation has been revised in accordance with the second German edition published at the beginning of the present year, and only a few alterations, necessitated by the advance of investigation, have been introduced. Of these, the most important is the section on uranium rays and radio-activity, which has been entirely rewritten by the author for this translation.

In revising the proof-sheets I have enjoyed the excellent co-operation of Mr. D. F. Twiss, M.Sc., to whom I would here express my sincere thanks.

<div align="right">A. F.</div>

Birmingham, *July* 1904.

PREFACE TO THE SECOND EDITION

THE fact that, in the space of three years, the four thousand copies forming the first edition were entirely exhausted, has given me the assurance that in spite of certain, in some cases passionate, opposition to the line of instruction set forth in this book, a large and increasing number of younger and older fellow-chemists believe, with me, in the suitability of these new methods. This impression was strengthened by the fact that the translations into English and Russian which have appeared have also reached a circulation which is to be numbered by thousands of copies. Translations into Japanese and French are also about to appear. Lastly, I believe that the same interpretation may be placed on the fact that in several text-books, both in German and in other languages, these new ideas have been adopted and applied by other authors.

I have, therefore, found no cause for making any essential changes in this book, although I have felt it to be my duty to subject the material to a careful revision, and, where necessary, to correct or amplify it. In the case of the introductory paragraphs I have again felt the desirability of rewriting them, and of developing the fundamental conceptions in a clearer and more concise manner.

In carrying out the revision I have enjoyed the excellent assistance of Dr. Herbert Freundlich, to whom I would here express my sincere thanks for his extensive and intelligent aid. In expressing my thanks to the numerous colleagues and fellow-chemists who have assisted me by the communication of printer's errors and of objections, I would also make the request that they will lend their valuable co-operation in the case also of this new edition. For such assistance I am

indebted more especially to my colleagues, Professors Abegg
Vater; as also to the translator of the English edition, Dr.
Findlay. Perhaps, also, I may hope that as the book passes into
quarters which have hitherto held themselves more aloof from
newer chemistry, criticism from the point of view of the requiren
existing there, may let me know the additions which may be neces

W. OSTWAL

TRANSLATOR'S PREFACE

In presenting the accompanying translation of the *Grundlinien der anorganischen Chemie* to English-speaking students, the translator hopes to be thereby contributing somewhat to a more wide-spread knowledge of the application of the more recent developments of General Chemistry, and consequently to a more just appreciation of their importance in the study of the other branches of the science.

In the present translation the mistakes which had crept into the German edition have been, as far as possible, corrected, and otherwise various minor changes have been made. As, however, these have all been made either at the author's suggestion or with his approval, special attention need not be drawn to them.

One change, however, relating to the nomenclature of the ions, calls for special mention. The terminology adopted in this translation, with the approval of the author, is that proposed by Professor James Walker, F.R.S. (*Chemical News*, 1901, **84**, 162). I would express my thanks to Professor Walker for his kindness in placing this nomenclature before me in time for its incorporation in the present translation.

The proof-sheets have all passed through the hands of the author, and I would here express my indebtedness to him for suggestions made while the book was passing through the press. My best thanks are also due to Messrs. R. S. Hutton, M.Sc., and Sydney A. Kay, B.Sc., for their invaluable assistance in reading the proof-sheets.

A. F.

University College,
  London, *January* 1902.

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PREFACE

THE first sketch of the present work dates back double the time designated by Horace as necessary for the maturing of a literary work, and some of the attempts to overcome the difficulties which were then met with have occupied me during the whole period of my activity as a teacher. The recognition that such a task is, by its nature, unlimited, and that it is possible to *round it off* but not to *bring it to a conclusion*, finally brought the resolution to maturity to give publicity to the accompanying attempt.

The task which hereby presented itself was to so incorporate the new notions and theories of scientific chemistry in the course of instruction that the student would, from the beginning, be made acquainted with the improved views instead of having first to learn the older, untenable notions, only to find out later that these must be abandoned. It was therefore necessary to considerably alter the fundamental form which is at present found, with slight modification, in the present text-books. I have endeavoured to do this only to such an extent as appeared to be demanded by the object in view, and have retained as much as was possible of the approved forms. If in this respect I have been too radical in my procedure for the feelings of some of my colleagues, it should be remembered that new cloth in old garments will not suffice here. On the contrary, a connected whole can be produced only when it is formed in its entirety by *one* mind and executed according to *one* plan.

I have retained, in the first place, the naturo-historical arrangement of the subject-matter. One could, perhaps, even now venture the experiment of constructing chemistry from the commencement a rational science on the basis of a few general principles, and introducing the description of the various substances only in illustration these general laws. I have been deterred from this by the

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of the historical connection, and by the recognition of the fact th
diversity of substances is too great and a knowledge of each of
too important to allow of such a method of treatment being mad
of for instruction at the present time. The course I have pu
therefore, is to insert the general laws in the traditional fra
the naturo-historical arrangement according to elements and
compounds, at those points where cause and opportunity for it
sented themselves. The task to be accomplished here has
resemblance to an artistic problem; for the insertion of the g
laws could not be left to chance occasions, but these laws them
had to follow a systematic arrangement which would ensure
comprehension and the recognition of their mutual conne
Accordingly, I cannot regard the solution attempted by me a
only possible one, and can imagine numerous other ways of atta
the end. It appeared to me, however, to be worth while to ende
to prove that such a course of instruction is possible at all

A text-book which pursues reformatory plans of the above n
appeals naturally to two kinds of readers—the teacher and the stu
and has therefore a double task to perform, which increases the la
not a little. In this connection I have always, in cases of doubt,
had regard to the requirements of the student, and have thereby
led to a certain fulness of treatment which would not have
necessary had I written exclusively for the teacher. If the latter
to take much that is "self-evident" along with the rest, he ha
the other hand, the convenience of finding the subject-matter alr
formed into shape, and only requires to modify it according to
personal views, without himself having to carry out the remouldin
the material for his pupils.

With regard to the student, I have felt myself pledged to
carrying out of the chief thought, viz.—to offer him a re
systematically arranged subject, strictly developed in such a
that for a comprehension of the new facts only a knowledge of
which has preceded is assumed, not of that which follows. To rer
the first study more easy, the discussions which in a first reading r
be omitted, either because of their being more foreign to the sub
in hand or because of especial difficulties, are marked with an aster
In all cases I have made it a rule to introduce general discussi
only when some readily intelligible facts furnished an example
which these considerations were to be applied. I have therefore
hesitated to return repeatedly to the same question whenever

appeared to me that its complete discussion at the point where it was first introduced would lead too far afield. The beginner, especially, I hope to have more than compensated for the loss of systematic exactness which such a method makes necessary, by the assurance of a greater familiarity with the subject.

For the carrying out of the rational construction of the chemical system, a method has proved suitable which, as has meanwhile appeared, was always applied by the recently deceased great master of chemical investigation and teaching, Robert Bunsen. It consists in giving a short summary of the chemical relations which are familiar to every one from his daily life, after the fundamental conceptions of chemistry have been established, but before the regular description of the substances and their transformations. This summary appropriately follows on the introduction of the conception of *chemical elements*. Not only does that conception thereby receive ample illustration, but the further advantage is obtained that where, as so often occurs, the necessity arises of mentioning substances which are treated only at a later point of the course, reference can be made to what has there been said.

I have exercised particular care in the development of the *conception of ions*. Sufficient attention is perhaps not paid to the possibility, the necessity even, of introducing this conception as a purely chemical and not as an electrical one. Even although, historically, it arose as the latter, its importance in chemistry depends essentially on its giving expression to the chemical fact of the *individual actions of the components of salts*, and it is in this sense that I have developed it. The facts of electrolysis and Faraday's law serve then only to widen and to deepen the conception obtained by a chemical method. I believe also that this is the way in which these views can be introduced even at a very early stage of chemical instruction, without making too great demands on the pupil.

In this connection I cannot refrain from expressing my conviction that, compared with formerly, the demands made on the intellectual coöperation of the student of chemistry must be increased. In proportion as chemistry develops from the condition of a descriptive to that of a rational science, it makes greater claims on the powers of thought and abstraction of its disciples. In this respect it approaches more and more to physics. Since, indeed, it is chiefly the same students who are at the same time learning chemistry and physics, the intellectual activity with which the student of physics is accredited

may also be claimed for the student of chemistry. I cannot conceal the fact that I have always been greatly grieved by the conscious descent to a lower intellectual stage which is so often found in elementary chemical text-books as compared with the text-books of physics or of mathematics designed for the same period of study. This circumstance is certainly to a great extent the cause of the idea which so readily arises among the younger physicists that chemistry is a science of a lower rank.

If the present-day chemistry, therefore, makes greater demands on the power of rational thinking, it also renders the purely memory work of mastering the subject considerably more easy for the student. The growth of the scientific interpretation and elucidation of the separate facts of chemistry facilitates in the highest degree the impression of them on the mind and their application, and at the same time affords an incomparably greater intellectual enjoyment than the study of the older, essentially descriptive chemistry could offer. From the experience gained from laboratory teaching during a number of years, I believe I may assert that it is just for those students who are endowed with some tendency towards independent thinking that the study of chemistry becomes both more easy and more living through its presentation in the modern spirit.

A few words ought also to be said regarding the fact that the intention of the present book is to be a text-book of *pure* chemistry. Regard has been paid to the related sciences and arts only in so far as *chemical* questions play a part in them. This holds in the first place for chemical technology, and also for medicine, agriculture, political economy, etc. The need of rendering more palatable the "in itself dry" material of chemistry by the addition of such matter has not been experienced by me, nor can I recognise its existence. The subject-matter of chemistry is dry only when it is limited to an enumeration of properties and to a collection of preparative receipts. So soon as it is treated in a truly *scientific* manner, each chemical compound becomes the centre of so much general and therefore interesting discussion that embarrassment is felt not on account of the lack but on account of the abundance of relationships. In proportion as any branch of study becomes more scientific, the necessity arises of restricting it to its own sphere.

course we do not here speak against the acquirement of a knowledge of the related sciences by the future chemist. But such knowledge will be all the more sound

the more it is acquired by special study directed to that object; for the indications, necessarily scanty and incomplete, to which a text book of chemistry must limit itself rather give rise to the danger that the student thinks he knows things of which he has on some occasion learnt such indications, and considers a closer study of them to be unnecessary.

Much might still be said to explain and justify the method of treatment wherein the present book differs from others written for the same purpose. The finding out and the criticism of these details, however, ought, I think, to be left to the expert teacher of chemistry. In the interest of the *student*, I have in all cases avoided a polemical discussion of opposing opinions; and although I am prepared to grant the possibility and probability of mistakes in the views which I have here given as appearing to me to be the most appropriate, I neverthe less believe that I may assert that these views are the outcome of careful consideration. The first three chapters, for example, were rewritten four and, in part, five times before they assumed the form which they now have. I would therefore beg the reader to believe, in cases where doubt may exist, that there was some special reason for the particular position adopted. This does not exclude but rather involves my readiness, in any given case, to honour any opposing views

May this book, then, which, in a certain sense, forms the coping-stone of a long course of active work pursued with affection towards the general introduction and extension of the new foundations of chemistry laid by Horstmann, Willard Gibbs, van't Hoff, and Arrhenius, achieve the good hoped for, and help to enlist and train new troops for the victorious march of our splendid science.

I cannot conclude these introductory remarks without remembering in gratitude the excellent assistance afforded me by Messrs. Böttger, Bodenstein, Brauer, Luther, and Wagner, in that they read the proof sheets and gave me much good advice both as regards the form of treatment and the subject-matter My special thanks are further due to Mr. Brauer for the preparation of the figures, — over one hundred in number, —which were specially drawn for this book. It will be easily seen that they are not diagrammatic, but sketched from apparatus actu ally put together ; they thereby form a considerable part of the didactic portion of the book relating to the performance of experiments

<div align="right">W OSTWALD.</div>

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER X

OXYGEN COMPOUNDS OF CHLORINE .

CHAPTER XI

BROMINE, IODINE, FLUORINE

CHAPTER XII

CHAPTER XIII

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CHAPTER XV

CHAPTER XVI

CHAPTER XVII

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CHAPTER XL

VANADIUM, NIOBIUM, TANTALUM, GALLIUM, AND INDIUM   .   .

CHAPTER XLI

TIN AND ITS CONGENERS   .   .   .   .   .

CHAPTER XLII

URANIUM, TUNGSTEN, AND MOLYBDENUM   .   .   .

CHAPTER XLIII

CHAPTER XLIV

CHAPTER I

GENERAL PRINCIPLES

1 **Bodies and Substances**.— In the outer world objects can be easily recognised having a definite spatial limit or form and distinguished by their properties from what surrounds them. Such objects are called *bodies*. Every body is characterised by the properties by means of which it can be distinguished from what surrounds it.

If we imagine a large number of bodies placed side by side and compared with one another, we can correlate them in various ways. We can consider their size and form, and arrange them according to these spatial properties, or we may neglect these and consider only the other properties; more particularly those *which are the same in every portion of the given body*. Such properties we shall call *specific*.

If we leave size and form out of account and arrange the bodies in such a manner that those which agree in their specific properties are placed in the same group, then the bodies are called *substances*. Thus the knife, the borer, and the various objects on the tool rack are so many different bodies. If, however, we leave the form thus out of account and consider them with reference to their other properties which are independent of the form, we shall call them the *same*, for they all consist of the same hard, heavy, and tough material called *steel*, which exhibits the same properties whether it is in large or small pieces. Steel is, therefore, the *substance* of which the above mentioned objects consist.

In the same way, every one will call the yellow, pulverisable lumps which burn with a pale blue flame, sulphur, no matter whether they are large or small, regular or irregular in form. Sulphur is the name of a substance.

The fact, now, that language possesses a fairly large number of names for different substances, is the expression of a general experience or of a law of nature. Just as in the case of animals and plants, so also *the different inanimate bodies can be separated into definite "species,"*

B

each of which embraces a large number of individuals or s
substances with concordant properties.   As is known, the numbe
species in the case of animals and plants, although, certainly,
large, is still incomparably smaller than the number of the individ
Likewise, the number of substances which differ in their prope
although large, is incomparably smaller than that of the single bo

This fact can also be expressed by saying that in the bodies t
do not occur all imaginable collocations of properties, but only ce
definite ones.   Every such collocation of properties which does n
occur, characterises a *definite substance*, and the fact that the bo
which occur in nature can be arranged in such groups or "substa
species," is the statement of an important law of nature, *the fundam
law of chemistry*.   It is the object of chemistry, as a science, to k
the properties of *substances*[1] and the relations which exist betw
them.

2. **Chemical Phenomena.**—Accordingly, since Chemistry d
with the objects and processes which make up the outer world, it fo
part of the *Natural Sciences*.   Although, in reality, there is only
Natural Science, extending over the whole range of phenomena,
the necessity of facilitating the survey of the whole extent of
knowledge had led, even at an early period, to the formation of
divisions, in which were grouped together phenomena more clo
related to one another, i.e. similar phenomena.   Such a subdivisio
formed by Chemistry.

The exact definition of the subject-matter of chemistry and of
boundary between it and the other branches of science related to
cannot be given at this point, since for this purpose there is necess
a knowledge of facts which have first to be given in this work.   S
it will simplify matters for the beginner to give him a token by wh
most of the chemical phenomena can be recognised, and which
therefore afford him guidance as to the direction in which he ha
give his attention.

We have seen that numerous *substances* can be distinguished wh
we consider their specific properties.   These substances, however,
not represent something that is unchangeable, for we often obse
that a body consisting of some definite substance undergoes *chang
i.e.* its relations to the instruments of sense by means of which
perceive it, and to its environment, are altered.   Such changes
be divided into two large, although not sharply defined, grou
Either they affect only one or some few relations and properties of

[1] As the result of an incompleteness in the use of language which, it is to be regrett
is very wide-spread, one often finds in text-books and papers that the two concepti
of body and substance are not kept rigidly separate, but are mixed up in such a w
that the word body is often used where substance is intended.   Descriptions such
"Sulphur is a yellow, brittle *body*" instead of *substance*, occur very frequently.   In t
book we do not always draw a sharp distinction between the two ideas, and it is desira
that the general scientific usage should, in this respect, also assume a more definite fo

body considered, or they are of a more radical nature, such that the body under consideration disappears, and its place is taken by other bodies having their own properties.

Phenomena of the former kind belong to *Physics*, those of the latter to *Chemistry*.

Take, for example, some definite body, such as a piece of sulphur. If we push it, it changes its place; it rolls over the table. None of its other properties, however, undergo change; it retains its yellow colour, its form, its weight, etc. Movement is therefore a *physical* phenomenon.

We can place the piece of sulphur in hot water, and it acquires thereby the property of producing the sensation of warmth when placed on the skin. No other change can be perceived. If we rub it with a cloth, it acquires the property of attracting light objects, such as scraps of paper; it has become electrified. Here, again, no other change in its properties can be recognised. These phenomena are, therefore, also to be assigned to *physics*.

We now bring the piece of sulphur in contact with a flame. It takes fire and begins to burn with a blue flame. The smell of burning sulphur, also, becomes noticeable, and if the burning lasts some time, the sulphur disappears; it is burnt. In this process not only do particular properties of the sulphur undergo change, but the sulphur disappears altogether, so that we can no longer see it at all. From the smell which arises at the same time, and which was not there before, we can conclude that something else has been produced from it. In this case, therefore, the sulphur has undergone a *chemical* process.

We recognise such chemical processes everywhere around us. The burning of petroleum and stearin in our lamps and candles, of coal in our fires, the transformation of food-substances in the animal organism, the processes connected with the germination and growth of plants, the rusting of iron, the turning sour of milk, the putrefaction of dead animal and vegetable matter, and innumerable other phenomena of a like kind, are identified as *chemical* through the disappearance of existing bodies and the appearance of new ones possessing other properties. To find out the laws of all these phenomena is the task of the science of Chemistry.

Experience. In describing the simple phenomena with which we have just been occupied, we have employed various conceptions and ideas of which we daily make use, and which are therefore familiar to us. For scientific purposes, however, we dare not rest satisfied with the somewhat indefinite and arbitrary notions which we attach to such concepts in ordinary life; their full purport must be examined and their meaning established with definiteness.

That which enters directly into the consciousness of a particular individual, is the changing conditions of his mind. We soon distinguish between the *inner* and the *outer* experiences: the former are

dependent on our will, the latter are not, or are so only indirectly. On account of this independence, we assume that such experiences have their cause in something that is different from our person, and the totality of these experiences we call the outer world.

All our experiences form a series of diverse states or processes differing among themselves. An event is never repeated in exactly the same way as it had once occurred.

Our relation to life would, therefore, be that of a wanderer in the darkness of an unknown and trackless region, if it were not that there are events which repeat themselves, not in their entirety, it is true, but still to a large extent. When we have experienced a number of such occurrences, we are in a position to foresee the probable further course of one of them when it recurs. If it is an event which influences our condition in some particular way, we are able to act so as to gain the greatest advantage, or suffer the least harm, from it.

The recognition of such events as in large measure repeat themselves, is called *experience*. It consists, therefore, on the one hand, in the recognition of the circumstances under which definite events occur, and, on the other hand, in our knowledge of the *course* of the events or of the sequence of their parts. .

4. **Conceptions and Laws of Nature.**—Not science only, but all mental life whatever, begins with the collecting of such similarities and the distinguishing of them from others. Even the brute does this when it seeks shelter in the thicket from rain or from a pursuer, because such action had before proved successful in similar circumstances. The most general relations of this kind are contained in language. Every noun, like "dog," or "stone," signifies that we are dealing with a large series of concordant experiences which present definite and always recurring similarities. For this reason the word sulphur signifies not, let us say, some one definite impression which I have once had at some particular time, but it is the summing up of repeated impressions in which can be recognised a group of different characteristics which always occur together. The sum total of the concordant characteristics—*those which are discordant being excluded*—is then gathered together in one such name.

Thus in the case of the word sulphur, I think of a yellow, solid substance, which can be set on fire, which becomes liquid at a not very high temperature, which sinks, without dissolving, in water, and becomes electrified on being rubbed. I do not think of sulphur as having a definite shape or size, but rather I denote by the name a piece of any size in which I recognise the properties mentioned. In the formation, therefore, of the name sulphur, there has by no means been taken into account the sum total of all properties of some definite single piece, existent or imaginary. On the contrary, no attention has been paid to the size, form, and origin of the single bodies to which I give the name of sulphur, but account has been taken only of the

specific properties, *i.e.* those which are found in all pieces, independent of these differences

Such an exclusion of differences in phenomena which in other respects are similar, is called *abstracting*, and the result of the abstraction, which in the more simple cases is condensed into one name, is termed a *conception*.

As is evident, one and the same phenomenon can be classed under different conceptions, according to the similarities of which we take account. The range of a conception, or the number of single phenomena which can be included under it, can be so much the greater, the fewer the points of agreement which are considered. At the one extreme are the single names which mark individuals, *i.e.* objects which are to be characterised as only of solitary occurrence. In this case we have very great variety, and generalisation consists only in the object always preserving essentially the same properties for a certain time—its period of existence.

At the other extreme are the general conceptions, such as "thing" or "object," in which emphasis is laid on no other property than on that, that it can be distinguished from other things.

Now, *the most important work of the sciences consists in the formation of suitable conceptions*. A *suitable* conception is, however, one under which is embraced as large a number as possible of single phenomena in such a manner as to contain the largest possible number of definite statements regarding each. The content of such statements is given by the *Laws of Nature*.

5. **Time and Space.**—One of the first things we experience, is the change of day and night, and the unbroken repetition of this change of light and darkness in our surroundings has therefore led to a fundamental conception, that of *time*. Since this change is quite independent of our will, we employ it as an *objective* measure of the events of our life, and refer these to the marks or signs which the change of day and night affords us.

For many occurrences this measure is too large. It is therefore divided into parts. The $\frac{1}{24}$th part of the day-and-night period, called the *hour*, is used as the unit in daily life. For scientific purposes, $\frac{1}{60}$th part of an hour, or the $\frac{1}{86400}$th part of the whole period, serves as the unit, and is called the *second*.

Experience also teaches us that innumerable differences in it can exist side by side *at the same time*. This diversity is con conception of *space*, in which are summed up all generalitie ties by means of which we can arrange and review co-exi

The diversity, which we call *space*, is a threefold (itself in the three dimensions—length, breadth, and hei, measurements are carried out either in one dimension length), or in two dimensions (areas), or in three (space or .

The unit of length is the length of a platinum rod pre

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repeated impressions in which can be recognised a group of
characteristics which always occur together. The sum to
concordant characteristics those which are discordant being
is then gathered together in one such name.

Thus in the case of the word sulphur, I think of a y
substance, which can be set on fire, which becomes liqui
very high temperature, which sinks, without dissolving, in
becomes electrified on being rubbed. I do not think of
having a definite shape or size, but rather I denote by th
piece of any size in which I recognise the properties ment
the formation, therefore, of the name sulphur, there has by
been taken into account the sum total of all properties of s
single piece, existent or imaginary. On the contrary, no att
been paid to the size, form, and origin of the single bodies
give the name of sulphur, but account has been taken o

as, temperature,
account of this
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that they can be
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experiment.

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Paris. This is approximately equal to the $\frac{1}{10000000}$th part of
earth's meridian, and was originally intended to be exactly equal
this. Since, however, two rods of this length can be compared w
each other with much greater accuracy than the ratio of one of th
to the earth's meridian can be determined, that relation has been, ve
wisely, discarded, and a considerable number of similar rods have be
made and compared exactly with the standard one.

These rods are kept at different places, so that should one or oth
of them by some mischance be destroyed, the unit itself would st
not be lost.

This unit is called a *metre*. It is equal to rather more than ha
the height of a man of average stature. For scientific purposes, t
metre is divided into 100 parts, called the *centimetre*, which in writi
is abbreviated to cm. Other divisions into decimetre and millimetr
of which 10 and 1000 respectively are contained in a metre, are bett
not to be used in science. When the magnitudes which have to l
expressed are much greater or much smaller than a centimetre, the
are written in the form $m \times 10^n$ cm. The indices most used are $+$
and -4. The length 100,000 cm. or 10^5 cm., is called a kilometr
a German mile is therefore nearly equal to 7×10^5 cm.[1] The leng
10^{-4} cm. is called a micron; it is one thousandth of a millimetre, an
is at the limit of the microscopically visible. It is also denoted l
the Greek letter μ.

The measures of *area* and *volume* are derived from the measur
of length, by taking as the unit of area and volume a square and a cub
respectively, the length of whose side or edge is 1 cm. The forme
unit is called a *square centimetre*, abbreviated sq. cm., the latter, a *cub
centimetre*, cc. These are the only units employed for the purposes o
pure science. In daily life and also in science, the *litre*, abbreviate
lit., which contains 1000 cc., and which is equal to the cubic conten
of a cube whose edge is 10 cm., is often used as the unit of volume.[2]

6. **Properties**.—The units which have just been defined serv
along with others, for the purpose of more accurately characterising th
properties of the different bodies and substances. Properties of sul
stances, or specific properties, are, for example, colour, density, powe
of refracting light, electrical conductivity, and many others. Thes
properties occur in a particular substance always in a definite manne
and to a definite extent. In future they shall be called shortly, pro
perties of the substance

Besides these, there are other peculiarities which can appear in

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[1] An English mile is nearly 160.93 f cm., or rather less than 1.61×10^5 cm. Tr
[2] The method of deriving the measures of area and volume with the help of the
square and the cube, is in no means necessary, nor is it the only one. For example
one could, so as not to change area, tetrahedron of 1 cm. side, a circle and a sphere
of 1 cm. radius or of 1 m. diameter. The choice of the square and the cube is, how
ever, probably the most suitable, since it allows of the easiest calculation of areas and
volumes from measurements of linear magnitudes.

body consisting of the substance considered, such as, temperature, electrical charge, pressure, illumination, etc. On account of this variability we shall call these, not its properties but its *conditions*. These differ from the specific properties in the fact that they can be imparted to the body or altered at will, without the substance passing into another, whereas the specific *properties* are always present when the substance is present.

The optical properties of a substance, *i.e.* its *colour*, and the manner in which it reflects light, or its *lustre*, are open to direct observation. That a piece of sulphur is yellow, and that the light is reflected to a fair extent from its surface, can be seen at the first glance.

I can learn, however, that the density of sulphur is greater than that of water, only when I place the piece of sulphur in water and note whether it floats or sinks; since it does the latter, I conclude that sulphur is denser than water. In what ratio, however, it is denser, can be learned only by making a quantitative experiment.

So it is also with the other properties of sulphur, to determine them, an experiment must be made. That is to say, we bring the substance into relations which are different from the ordinary, and note its behaviour under these new conditions. In this way we learn that sulphur is a non-conductor of electricity, when we touch a charged electroscope with a piece of sulphur, and find that the gold leaves do not fall together, or when we connect a galvanic cell with an electric bell, and find that the bell does not ring when we insert a piece of sulphur in the circuit. Further, by heating a piece of sulphur in a glass tube, we learn that it melts or passes into the liquid state at a not very high temperature.

The last mentioned experiment, the melting of sulphur, represents a transition to a group of other properties which are characterised by the fact that the nature of the substance itself undergoes change, which it did not do in the former experiments.

The *combustibility*, likewise, of sulphur when heated in the air, is such a property. Further, if we mix some sulphur with iron powder and heat the mixture in a test-tube, a thin walled glass tube closed at one end, it suddenly becomes incandescent, and when cold, both the sulphur and the iron are seen to have disappeared, and in their place a black substance has been produced with quite different properties.

Processes in which certain substances disappear and other ones are produced, have already been designated as *chemical*, in contradistinction to the *physical* or those in which the substances maintain their existence. We shall, therefore, divide the properties of a given substance into physical and chemical; the former being those we observe when the substance remains unchanged, the latter being seen when the substances are converted into others.

* The question is often raised, whether processes such as fusion, when the temperature is raised, or solution in a solvent, are to be

regarded as chemical or as physical. Disagreement, however, on this question is without point, since nothing of an essential nature depends on the decision ; for this, evidently, is of consequence only with regard to the arbitrary plan of treatment. If we retain the definition already given, we shall recognise that sulphur with its specific properties certainly disappears when it is made to assume the liquid state, by heating or by treatment with a solvent. It therefore undergoes a chemical change. Many, however, designate such changes as physical, since it is easy to recover the sulphur in the solid form with all its properties, by lowering the temperature or by evaporating off the solvent. But a substance which has undergone chemical change can, in general, also be again obtained from the new substances produced, although more complicated methods are often necessary. It will, therefore, on the whole, be better to class these changes along with the *chemical*.

7. **Homogeneous Substances and Mixtures.** —Whereas in everyday life, for the purpose of characterising a substance, we make use of those properties which appeal to our senses, and which allow only of making rough distinctions, it is the task of chemistry to ascertain with all possible exactness all the properties which can be employed for the characterisation of a substance in the sense in which we have defined it. This is possible, however, *only when every part of the substance has exactly the same properties as every other part.* If we consider, for example, a piece of granite, we readily convince ourselves that this stone is made up of parts having different properties. Beside the white, very hard grains there are others which are less hard and of a reddish colour, and between these there are rather soft, lustrous laminae. In determining the properties of such a body, various results would therefore be obtained, according as the one or other small piece was examined.

We cannot, therefore, designate granite as a substance in the chemical sense, but rather as *a mixture of different substances.* As the characteristic of a substance in the chemical sense, we must demand that all portions into which it can be separated, exhibit the same properties. Such substances are called *uniform* or *homogeneous.* According to this, *chemistry is the science of uniform* or *homogeneous substances.* Simple as this conception appears, it required a long time —a time to be reckoned by centuries— for it to be formed with sufficient clearness, and the older history of chemistry as a science, might be called the history of the labours in the working out of this conception. The difficulty lay essentially in the fact that a sufficient distinction was not made between *mixtures* and homogeneous substances, with the result that the regularities which are peculiar to the latter but not to the former, could not be discovered.

8. **The Exactness of the Law of Properties.** The statement that sulphur is denser than water, and that it melts at a moderate

temperature, can be made in a much more definite form by stating in what ratio the density of sulphur is greater than that of water, and at what temperature the fusion of sulphur occurs.

In a like manner, many other properties, and especially physical properties, can be expressed in definite measure, and the question arises, how do different samples of the same substance behave when a quantitative determination of their properties is made.

One might imagine that substances behave in a manner similar to the species of animals and of plants. The different specimens of one species, say the common mouse, resemble, it is true, but do not completely agree with one another in size, growth of hair, colour, shape, etc. On the contrary, within certain limits, they show differences with regard to their properties. In like manner one could assume that the properties of different specimens of the same substance have closely approximate values—that these values, however, are not quite definite but vary within certain limits.

The innumerable investigations of this point which have been undertaken, show that the law of properties of substances holds not only approximately but *exactly*, and, therefore, *the measurable properties of different specimens of the same substance agree not only approximately but with all exactness.*

It must be at once emphasised that it is not intended here to assert the *absolute* validity of the law. The absolute can never be the subject of experience, and, in fact, it is not admissible to employ the word absolute with reference to any relationship based on experience. The meaning of the assertion is rather this, that experience has, so far, shown no deviations which are beyond the limits of the possible error of observation. For, every measurement is exact only within a certain limit, and all conclusions which are drawn from these measurements can be valid only to this limit. Thus, the density of sulphur can be determined only with a limited degree of accuracy, and if the same value has been obtained with different specimens, the identity can be asserted only to this limit. The meaning of the assertion that the properties of different specimens of the same substance are the same, is only this, that within the limits of error hitherto reached, no differences have been found.

The accuracy with which a magnitude is known must always be expressed in *fractions of its value*, and not as a concrete number. If in the measurement of a length the possible error amounts to 0·1 cm., this may express a large or a small degree of accuracy, according as the length is long or short. If we measure a distance of 20 metres to within 0·1 cm., the measurement is very exact, for the error amounts to, at most, $\frac{1}{20000}$th of its value. On the other hand, if a length of 1 cm. is known with such a limit of error, the measurement is not very exact, for the error can amount to $\frac{1}{10}$th of the measured value.

9 Pure Substances and Solutions.—To the law which has just

of liquids, in so far as they are not bounded by rigid walls, appr
the form of a horizontal plane.

Gases have neither a definite form nor a definite volume; th
completely every vessel into which they are brought.

All these relations are further subject to special laws, whic
be discussed in their appropriate place.

By means of the characteristics we have just given, we shall
as a rule, no difficulty in determining whether a body is solid, l
or gaseous. If a body, when placed on a plane, retains its shape
solid; if it spreads out while, at the same time, a bounding pl.
surface, is formed on the top, it is a liquid; if it exhibits in no
tion a bounding plane of its own, it is a gas. Between these
physical states there are, it is true, intermediate states which
times render the decision difficult; still these are not very frec
and for the present we need not discuss them in greater detail.

A given body does not under all circumstances remain i
physical state in which it is at a given time; the physical
depends especially on the *temperature* In this case, the genera
holds that *with rising temperature, a solid substance can become liqu
gaseous, and a liquid one gaseous, but never the converse.* On the
hand, with lowering of temperature, gases become liquids or s
and liquids become solids.

Although the sense in which the change takes place canno
departed from, the liquid state need not, however, appear as an i
mediate state between the gaseous and the solid. On the cont
cases not unfrequently occur where with rise of temperature, s
pass directly into gases, and by cooling, gases pass directly
solids.

The laws which these transformations obey, will be discu
later (Chap. VII.)

15. **Summary.**—The conception of *substance* has been devel
By this name are designated the classes into which the inanimate b
can be arranged according to their properties. Experience tea
that it is possible to arrange the naturally occurring or the artific
prepared bodies in classes so that the individual members of a
have the same specific properties. By properties in this sense
understood only those which are essential, and which cannot be g
to or taken from the body at will. Experience teaches further
different bodies which belong to the same class or which consis
the same substance, agree not only approximately but *exactly* in
properties, so that the value of any property determined on
specimen may confidently be expected to be found in all specimen
the same substance.

*The law of nature that classes can be formed of bodies which a
entirely with one another in their essential properties, is the fundamental
of chemistry.*

is identical in substance only when they show entire agreement in *all*
their specific properties, the task of testing whether two substances
are the same or not, appears impracticable. And still, chemists are
used to identify substances with certainty after testing some few
properties.

The surmounting of this difficulty is rendered possible by the
fundamental law of chemistry already given (p. 2). This law, in its
application to the present question, can be stated thus: *When two
substances agree entirely in some few properties, they agree also with regard
to their properties.*

This law, like all other laws of nature, is only a summary of
observed facts. It does not *prescribe* that something *shall* happen, but
indicates what relations exist. For this reason the term "law,"
borrowed from jurisprudence, is not very suitable for expressing
such regularities in natural phenomena, and it can be used without
disadvantage only when the distinction, to which we have just drawn
attention, between a law of nature and a civil law has, once for all,
become quite clear.

11. Induction. The total number of cases classed under a law of
nature can, evidently, be divided into two groups: a small one, em
bracing the cases which have been tested, and a very large one, to
which belong the cases which have not been examined. For the task
of testing a law in *all* cases in which it applies could not be under
taken, as the labour involved would be too great.

But, indeed, the necessity for such an examination is not felt; for,
from the fact that in all cases which have been observed the law has
proved valid, we may conclude with a high degree of probability
that it will hold equally in those cases which may in future be investi
gated. This probability becomes all the stronger as the number of
cases investigated increases, and the more the cases chosen for ex
amination are independent of one another.

When the universal validity of the relationship has been estab
lished with a definite measure of probability, we are accustomed to
regard it as a *law of nature*. However, the history we have just given
of the genesis of such a law, implies that it cannot have the character of
certainty, and it is quite possible that, following on the many con
firmatory cases, some should be found which do not conform to the
law. The procedure which we have to adopt in such cases will be
discussed later. For the present, we accept the statement that the
laws of nature are conclusions as to probabilities, based on experience.

Such conclusions are called *inductive*, and the procedure by which
they are obtained is called *induction*. The whole of natural science is
made up of such inductive conclusions.

Sometimes the need has been felt of placing the laws of nature
on a more certain foundation than is furnished by conclusions by
analogy based on experience, since these afford no protection against

16. Changes of Weight in Chemical Processes.—If we choose out for close investigation some of the innumerable chemical phenomena which occur daily around us, we are struck with the *changes in the weight* of the substances taking part in the chemical process. When the stearin of a candle or the petroleum in a lamp burns, these substances seem to disappear entirely; the wood or coal burning in the furnace leaves behind only $\frac{1}{50}$th to $\frac{1}{20}$th of its weight of ash. On the other hand, the sulphuric acid manufacturer obtains about three kilograms of sulphuric acid for every kilogram of sulphur converted. Changes of weight are therefore connected with chemical processes, and we have now to ask whether any generalisations can be made regarding these.

The examples we have just cited appear only to lead to the conclusion that in chemical processes diminution as well as increase in weight may occur. These are, however, not suitable examples for deciding the question, for the processes take place with the substances in free communication with their surroundings, especially with the air, and do not therefore allow of a balance being drawn up. To achieve this we must conduct the experiments in a closed space.

17. Experiments.—At the bottom of a large, thin glass flask (Fig. 2), and resting on a layer of asbestos, is a small dish containing a little phosphorus. Phosphorus is a substance which requires only a slight elevation of temperature to cause it to take fire. The flask, closed by a ground-in stopper, is accurately counterpoised on the balance. The part where the phosphorus rests is then warmed, and the latter at once takes fire. In a short time the phosphorus becomes extinguished, whilst the flask has become filled with dense, white fumes.

on again placing the flask, after it has become cold, on the balance, ____ ___ __ ___ ___ __ _____

The flask must be allowed to cool before being reweighed. So ___ __ __ is warm it warms the air surrounding it, and this, ascending, ____ the flask slightly upwards, and makes it therefore appear too __

Secondary circumstances of a similar nature, which more or less affect the result, are always met with in carrying out quantitative experiments. If an exact result is desired, they must be known and ____ ___ either obviated or, if this is not possible, taken into _____ The real difficulty of exact measurement lies in these _____ influences, and only by a varied experience, obtained by _____ the experiments under as many different conditions as _____, can one succeed in so controlling these influences as to obtain ____ measurements. Compared with this, the carrying out of the ____ measurement is generally an easy matter.

The fact just described, that when combustion takes place in a ____ space no change in the total weight is observed, although ____ substances disappear and others are ____, is a general one. No matter what _____ are burned under these conditions, a ____ of weight never occurs. This law also __ ___ restricted to combustions alone, but is ____ ___ chemical processes. To illustrate this __ ___ perform the following experiments.

A wide test-tube is placed in a conical flask ___ ___ mouth (an Erlenmeyer flask) (Fig.

Two substances which, on contact, react

FIG. 3

_____ with one another, are placed, one in the conical flask, the ___ in the test tube, so that they are kept separate. The flask

having been carefully closed and its weight determined, the substances are brought into contact by tilting the whole apparatus. Chemical reaction then takes place, generally accompanied by rise of temperature. On placing the apparatus, after cooling, again on the balance, *its weight is seen to be unchanged.*[1]

Another method of performing this experiment ____ in Fig. 4. This method is more convenient, but the two

____ _____ substances which give rise to chemical reactions recognisable by _____ ____ __ ____ mostly a concentrated solution. Potassium carbonate ____ ____ white precipitate; silver nitrate and caustic potash (brown) back _____ __ __ ____ and sodium sulphide (orange-red precipitate), zinc _____ _____ and clear solution; silver nitrate and ferrous sulphate, again ____ ____ ____ hydrochloric acid and zinc; and (separation of volume) chloral ____ ____ and potash (formation of two liquids).

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divisions. Of these, the ones most employed are the kilogram, which is equal to 1000 or 10^3 gm., and the milligram or 10^{-3} gm. The other magnitudes (decagram = 10 gm., hectogram = 100 gm., decigram = 0·1 gm., centigram = 0·01 gm.) are but seldom used, and for scientific purposes should never be used at all.

For the chemist, now, neither the question, how much kinetic energy a body acquires under a given velocity (the mass), nor the question, what force it exercises on its support (the weight), is of supreme interest. An explanation is therefore necessary as to why the balance is, rightly, called the most important instrument in scientific chemistry.

When we buy substances for chemical purposes, for example, coal or food, which is of course done by weight, the mass and the weight
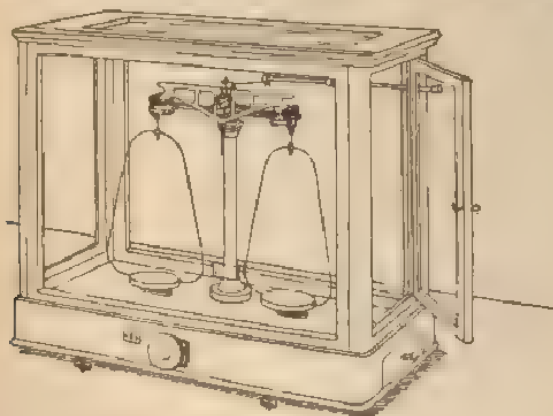
FIG. 5.

of these things have likewise no direct interest for us. The determining factor is *that the chemical values*, the nutritive value or the heat that can be obtained by combustion, *are also proportional to the mass and the weight*. These values are all energy magnitudes. In mass and weight, therefore, we have a measure of the chemical energy, or the work which the bodies can do by chemical transformation; and we determine the weight when we wish to measure the amount of chemical effect. How this is done in detail will be discussed later (Chap. VIII).

* The chemist's balance (Fig. 5) is a lever with two equal arms. Weighing consists in allowing the body whose weight is to be determined, to act on one end of the lever, while differ   ts of known value are made to act on the other end, until equi   stablished, or until the lever turns neither in one direction   er.

* The balances used in ordinary life differ   nly in *sensitiveness* from those used for scientific purposes   nary kilogram balance will still show differences of 1 gm   s.,

the best scientific balances, when loaded with 1 kilogram, will show a difference of one hundredth of a milligram, or 0·00001 gm. The former has therefore a limit of error of 0·001, the latter of 0·00000001. The latter therefore allows of the determination of weight and mass ratios with proportionately greater exactness.

* This increase in the sensitiveness of the balance is effected by minimising, as far as possible, the hindrances to movement due to friction. The axis of rotation of the beam of the balance is formed by a knife-edge made of hard steel or agate, resting on a plane of hard stone. In the same way, the axes from which the pans for the weights and for the body to be weighed are suspended, are formed by knife-edges resting on planes. The three knife-edges must be parallel to one another and in the same plane.

* To prevent the knife-edges from wearing away too rapidly, they must be allowed to rest on the planes only during the time the balance is being used. Every good balance is therefore furnished with an arrangement for "arresting" it. This is so made that by turning a knob or a handle, the scale pans are first raised from the end knife-edges, and then the beam from the plane on which it rests. The weights, etc. are placed on the scale pans while the balance is "arrested." On slowly "releasing" the balance, it can be seen in what direction the balance turns, and whether the weights have to be increased or diminished.

* Since a moderately good balance detects amounts even as small as 0·0001 gm., one would require weights of a corresponding value, in order to finish the weighings. These are very inconvenient to handle, and chemical balances are therefore furnished with another arrangement for determining the smallest weights. The balance beam, from the middle to the end knife-edges, is divided into ten parts, and there is a contrivance by means of which a weight of 0·01 gm., which from its form is called a "rider," can be placed at any point on the beam. According to the law of levers, the effect of the weight is smaller, the nearer it is placed to the axis of rotation. If, for example, the rider is placed at a distance from the axis equal to ⅒ths of the length of the beam, it acts as a weight of 0·003 gm., and every tenth of the beam corresponds to one milligram.

* In weighing, therefore, it is necessary to counterbalance a body only to within 0·01 gm. with weights, and then to move the rider till complete equilibrium is obtained. The tenths and hundredths of the beam length give the milligrams and tenths of a milligram which have to be added to the weights.

* The production of equilibrium is shown by a pointer attached to the beam of the balance and moving in front of a scale. Since a good balance does not remain at rest but continues for a long time oscillating like a pendulum, one observes the extreme positions of the pointer, or the deflections, and takes the mean of these

* To complete the weighing it is not expedient to obtain the final adjustment by shifting the rider, as we have just assumed for the sake of clearness. Rather use is made of the fact that the change of the position of rest is proportional to the excess of weight. If the change of zero caused by a change in the weight of 1 milligram has been determined, it is only necessary to set the rider at the nearest whole tenth to be able to calculate from the deviation of the point of rest now obtained from that when the balance is unloaded or the zero, the fractions of a milligram which would make the equilibrium perfect.

Density and Extensity. — The aids to the definition and measurement of masses and weights just considered form the basis for the determination of an important property possessed by all substances, which, on reason of the great variation of its value from substance to substance, is largely used for distinguishing and characterizing these. This is the *density* and the *extensity* (inverse).

When defining the conception of "substances," we expressly omitted to take the mass into account up to as also the space occupied by a given piece of the substance. Since, however, these two magnitudes vary simultaneously and in the same degree, their ratio is a definite property of the substances, and according to the general law must always have the same value for a given substance under given conditions.

If we denote the mass of a given specimen of a substance by m, and the space which it occupies, or the volume, by v, we can form the two expressions m/v and v/m. The former, the mass in unit volume, is called the *density* or the *specific gravity*; the latter, the volume of unit mass, is called the *specific volume*; we will call it the *extensity*.

The units in which these magnitudes are measured have already been defined. The unit of mass is the gram, and that of volume is the cubic centimetre. Since the mass is expressed by the same number as the weight, the density is equal to the weight of the body in grams divided by its volume in cubic centimetres; hence the name *specific gravity*. The extensity has the reciprocal value. If we call the density d and the extensity e, we have the relation $d = 1/e$ and $e = 1/d$.

Of these two expressions the density has, as a rule, the preference, for, on viewing a body we first estimate its volume with the eye, and obtain an idea of its weight only when we have taken it in the hand. One refers, therefore, involuntarily, the weight to the volume and not the volume to the weight. For scientific purposes it is better to consider the opposite relation. For the mass is an unchanging magnitude in a body, whereas volume depends on pressure and temperature, and it is more rational to refer the variable quantity to the changing than conversely.

In accordance with the common custom, however, the densities here also receive the foremost place.

27. **Measurement of Density and Extensity.**   To determine the ratio between volume and mass, a measurement of both magnitudes for the given body is necessary.   The mass is determined by weighing (p. 25); the determination of the volume varies with the physical state of the body.   It is easiest in the case of liquids.

The most direct method consists in filling a vessel of known capacity with the liquid, and determining its weight.   Such vessels can be made of various kinds according to the accuracy aimed at.   A very rapid and convenient method consists in the use of a vessel of the form shown in Fig. 6, called a *pipette* (small pipe)   It consists, essentially, of a narrow tube, widened in the middle, and is filled by dipping one end in the liquid and sucking at the other.   On the upper tube is a circular mark forming the limit of a definite cubic content, which usually amounts to a round number of cubic centimetres.   In

Fig. 6.

filling, a slight excess of liquid is sucked up, and then, closing the upper end of the pipette with the index finger, the excess is cautiously allowed to run out till the liquid stands at the mark.   The filled pipette is placed on the balance in a horizontal position, resting on a bent wire carrier (Fig. 6).   If the empty pipette with the carrier has been previously counterpoised, the increase in weight gives directly the weight of the liquid.

The determination is simplest when a pipette of exactly 1 cc. capacity is used, and a weight made which counterbalances the empty pipette along with its carrier.   In accordance with commercial use, such a weight is called the *tare*.   The extra weight is then directly equal to the density of the liquid, since, of course, the divisor, the volume, is equal to 1.   Such a determination can be carried out with an error which is less than 0·001.

Another method is based on the principle of Archimedes, according to which a body sunk in a liquid experiences an upward pressure equal to the weight of the liquid displaced.   A glass sinker, closed on all sides and hung by a hair or fine platinum wire, is counterpoised on the balance; it is then sunk in the liquid to be investigated, and the decrease in weight, or the upward pressure, determined.   The volume of the sinker is determined by conducting the same experiment in water; the upward pressure in grams is equal to the volume in cubic centimetres (p. 23).   If this experiment is not performed at 4° C., one finds from the tables of the expan   f water the weight of 1 cc at the temperature of the experime   vides the upward   re found by this.

In this case also it is m   t to make a volume is exactly   l to   The loss (

then, directly (in the case of 10 cc. after moving the decimal point one place to the left), the density of the liquid.

Finally, for rapid determinations of the density, the *hydrometer* is used. This consists (Fig. 7) of a glass float terminating at the top in a narrow tube within which there is a scale. The instrument is so made that it floats perpendicularly in the liquid to be investigated. Since a floating body sinks to such a depth that the weight of the liquid displaced is equal to the weight of the body, the position of rest varies with the density of the liquid, and the scale is read at the point where the stem passes through the surface of the liquid. The scale is generally graduated so as to allow of reading off the densities directly. However, other scales are in use which have different names according to their inventors, and whose zero corresponds to the density of water. For scientific purposes these have no importance.

28. Densities of Solid Bodies are determined by two chief methods. Generally, they are weighed first in air and then in water or other liquid. The first weighing gives the mass, the second the loss of weight or the upward pressure, and from that the volume. When the second weighing is carried out in water, the upward pressure is equal to the volume (the influence of temperature being allowed for; *vide supra*). If another liquid must be used, as in the case of substances soluble in water, its density must first be determined by one of the methods just described, and the upward pressure must be divided by the value of this. For the volume of the liquid is equal to its weight divided by its density (p. 27).

In carrying out such experiments, regard must often be had to the fact that the bodies are not present in large pieces, but in grains or small pieces. In this case they are weighed under water in an open vessel of glass or platinum, as in Fig. 8. The weight of the vessel under similar conditions, viz., immersed in the liquid, must, of course, be previously determined.

Another method, employed especially with small quantities, consists in mixing together two liquids, one of which is denser, the other less dense than the solid to be investigated, so as to give a liquid whose density is equal to that of the solid body. This identity is shown by the fact that the body neither rises nor sinks, but remains suspended in the liquid. The experiment is carried out by placing the body first of all in a small quantity of the lighter liquid, in which it sinks to the bottom. There is then cautiously added so much of the other liquid till the suspension is produced. Generally one will

add rather too much of the second liquid ; the error can, howev
easily rectified by the addition of some of the lighter liquid.

When suspension takes place, the density of the mixture is
mined by one of the methods described on pp. 28 and 29.

* As a heavy liquid there is used methylene iodide or ace
tetrabromide , as a light one, benzene or toluene. These liquid
be obtained commercially.

The necessary information for the determination of the dens
gases will be given later (Chap. V.).

29. Influence of Pressure and Temperature on the Den

It has already been mentioned that although the mass exper
no change in any process, the volume is dependent both o
temperature and on the pressure. The density of a substance
therefore likewise vary with these circumstances ; and in ord
make a statement definite, the values of both of these must be
at the same time.

The influence of pressure, now, is generally very small. The v
of liquid substances is diminished only by some hundred thousa
of its value when the pressure is increased by 1 atmosphere, a
the case of solid bodies this influence is in most cases still smaller
is therefore necessary to have regard to this variability only i
case of very exact investigations

The influence of *temperature* is, however, much greater.
volume of a given body is (with few exceptions) increased by a r
temperature. The amount of increase is very different in the ca
different substances, and is in general greater for liquids tha
solids. As a rough estimate one can assume that liquids expan
about one thousandth of their volume for every degree of rise.
is, however, only a very rough approximation, since the am
varies not only from liquid to liquid, but also with the temper
itself. The higher the temperature, the greater is the relative inc
of volume with the temperature

In the case of accurate statements of the density of liquids, t
fore, a statement of the temperature is necessary. Approxi
statements, such as will often be made in this book, refer to
temperature say 18 C.

30 The other Kinds of Energy. In the discussion of perfect

imperfect machines (p. 21), there still remains the question, What bec
of the work which in imperfect machines disappears ? In order to
an answer to this, let us make a machine which is *as imperfe
possible*, so as to make the effect produced by this quality as clea
possible. In other words, we increase the friction to such a de
that the machine consumes almost all the work that is put into it
gives out only a small amount of it in external work

The result of such an increase of the friction is seen in the cas
badly kept axle-bearings in driving-engines, vehicles, etc. Those p

mercury not of oxygen. Since a substance is characterised only by its properties, such a statement as the above has no real meaning, and is only a short inaccurate method of expressing definite regularities which will be discussed later (Chap. IV.).

This method of expression is, however, so generally used that we must retain it for the sake of intelligibility, though with the reservation just made.

38. Combination.—The process of the conversion of oxide of mercury into mercury and oxygen can be reversed. By heating mercury in contact with air, i.e. with the oxygen of the air, to about boiling point, it is converted into oxide of mercury. The process, however, requires days in order to yield an appreciable amount of oxide of mercury.

As a single substance is hereby produced from two different substances, the process is called a *combination*, the reverse process, the conversion of one substance into two—oxide of mercury into mercury and oxygen—is called a *decomposition*. In the same way, mercury and oxygen are called the *constituents* of oxide of mercury, and it is a *compound* of the two other substances. It is looked upon, that is, as a *composite* substance with regard to its constituents; still we may be again reminded of the reservation we have just made.

39. Quantity Relations.—Returning to our experiment, we can now the question as to the quantity relations of the participating substances. From the experiences of common life, one will be inclined to assume that in the conversion of a substance A into a substance B, the amount of B obtained will diminish and increase in the same ratio as the amount of A used. However, from the same experiences, one would conclude that although the "yield" would on the whole agree with this rule, it would, in individual cases, show more or less deviation from it.

Let us perform suitable experiments by decomposing various accurately weighed-out amounts of oxide of mercury and measuring the oxygen evolved. (The necessary precautions to be taken here will be presently discussed; *vide* Chap. V.) We find that *the ratio of the amount of oxide of mercury used to the amount of oxygen obtained is constant, not only approximately but with all the accuracy with which we can make the measurement.*

The relation which we here meet with is a case of a general law of nature.

When one substance is converted into another, there exists a definite, invariable relation between the weight of the substance disappearing and that of the substance produced.

We can at once extend this law and say that when two substances combine with one another to form a third substance, an invariable relation also exists between the two substances. For the weight of the substance produced stands, in accordance with the law just stated,

feasible to create work out of nothing, and that machines at be
give out only the amount of work which is put into them, we
the positive *law of the conservation of work* in perfect machines.
further question as to where the lost work remains in imp
machines, has led to the recognition that work can be converted
other forms of an equivalent thing, which is called energy ; and
final result of the impossibility of perpetual motion there is deve
the law of the conservation of energy   one of the most imp
laws of all natural science

* Similar developments of fruitless labour into positive law
be recognised in other parts of natural science, and we shall at a
time have to occupy ourselves with such cases (cf. Chap. IV.).

31. **Summary**. The production and disappearance of subst
during chemical processes raises the question, whether these ch
obey any laws ; and it is found as a universal experience, wit
exception, that the total *weight* of the substances taking part in
chemical process remains unchanged. The total weight of the
substances produced is equal to the combined weight of the
stances disappearing.

There holds, therefore, for all chemical processes (and for all
known processes likewise) the *law of the conservation of weight.*

The *mass* of a given body is proportional to its weight, the
of mass to weight being, for all bodies, independent of their
properties, constant at a given spot. Hence there also obtains fo
processes, the chemical ones included, the *law of the conservation of*

The two magnitudes, weight and mass, have no direct rela
to one another, and the law of their proportionality is a pu
empirical law.

An indirect relation between mass and weight is found by the
of the conception of work. Denoting by this name the product
force and the distance over which it acts, the law can be stated,
the simple "machines," that in the limiting, ideal case, the w
can be neither increased nor diminished by such machines. Th
exists, therefore, for them a *law of the conservation of work.*

In special cases, work apparently disappears. In these case
can always be shown that something else is produced at the s
time which is proportional to the work which has disappeared,
which can be reconverted into work. If we denote all such thi
as can arise from and be converted into work by the name *energy,*
if we measure the different kinds of energy in units based on
conversion of a definite amount of work taken as the unit, there h
good, quite universally, a *law of the conservation of energy.*

There are various kinds of energy. Besides work in the se
just denoted, *kinetic energy, electrical energy, chemical energy, heat,* w
characterised as various kinds of energy.

The unit of energy is called the *erg.* It was defined as twice

energy contained in 1 gram of any body when it has the velocity of 1 centimetre in 1 second.

If the body has the mass m and the velocity c, both measured in the units just given, its kinetic energy is equal to $\frac{1}{2}mc^2$.

When 1 gram falls through 1 centimetre, under the influence of gravity it acquires the velocity of 44.26 cm. sec. Its kinetic energy is therefore, equal to 980 ergs. This has been produced from the work of gravity, which is equal to the product of the force of gravity and the distance. Since the latter is equal to unity (1 cm.), the former must be equal to 980. The force with which gravity acts on 1 gram is, therefore, equal to 980 units.

A body of n grams on falling through 1 cm. acquires the same velocity since, as experiment shows, all heavy bodies fall equally fast. Its kinetic energy, therefore, amounts to 980 n. Accordingly, the force of gravity acting on n gm., amounts to 980 n units.

In view of it, weight and mass have a special importance, from the fact that the chemical energy which can be obtained by the transformation of any substance, is proportional to its weight and its mass. Since the value of substances used for chemical purposes, e.g. articles of food or fuel, are measured according to the amount of chemical energy which can be obtained from them, the weight is also a measure for the chemical value of different quantities of the same substance.

In conclusion, we may group together the units we have selected for the measurement of the different magnitudes. These units are naturally used in science, and are called *absolute units*.

Unit of Time	Second	sec.
,, Length	Centimetre	cm.
,, Mass	Gram	gm
,, Energy	Erg	e.

The first two units are not independent of one another since, when one of them is given, the other can be determined from it with the help of the first two.

From these fundamental units, compound units are derived by using the proper magnitudes. Thus, the unit of velocity is the velocity of 1 centimetre in 1 second, 1 cm. sec. The unit of force is that which acting over 1 cm. performs the work 1 e., and is therefore measured by 1 e. cm. It is called a *dyne*. The units of area and volume are given by cm.² and cm.⁴ The unit of density is 1 gm. cm.⁻, and of extensity 1 cm.⁻ gm.

The formation of compounds from their constituents takes pla. definite proportions by weight, which depend only on the nature of substances, and not on the circumstances under which the compo are produced. *This law of constant proportions by weight holds fo kinds of chemical transformation whatever.*

The exactitude of this law is of the same order as that of the of conservation of weight in chemical processes, *i.e.* no deviations it have as yet been proved.

Is Increase of Weight on Combustion Universal?—

Since the first supposition, that combustion and decrease of weight always hand in hand, does not turn out to be true, one may suppose that the opposite is the case, i.e. that increase of weight always occurs. For it follows from the law of conservation of weight, that burning petroleum and burning alcohol do not disappear into nothing. New substances must, therefore, be produced, and the following experiment will readily convince one of this. Take a large, dry tumbler and hold it over a flame so that the flame burns inside. The tumbler is then seen to become immediately covered with a film which has exactly the appearance of the film of moisture which forms on cold window panes. One closer investigation one can convince oneself that the film consists of water. Since this phenomenon does not occur when the tumbler is held over the unlit lamp, it follows that water is formed in the flame.

Further, if a similar tumbler be rinsed out with lime-water and then held in this condition over the flame, a white solid is formed in the lime-water which looks exactly like chalk. This phenomenon also occurs only when the lamp is lit.

The lime water for this experiment is prepared by shaking lime with water, and then allowing the milky liquid to stand in a closed bottle. In a few hours the lime sinks to the bottom, and the clear, transparent liquid is then poured off into another bottle. As a rule, merely again becomes milky, and must stand some time to become clear.

These experiments show that, although in the combustion of the two liquids, the latter certainly disappear, new substances are produced, which escape direct observation only from the fact that they occur as gases.

Processes, by means of which the presence of certain substances are detected, such as the formation of the film on the tumbler and the white solid in the previously clear liquid, are called reactions, and the substances necessary for them, reagents. The formation of the film is a reaction for water vapour, and lime water is a reagent for another substance which is also formed in the combustion of petroleum and alcohol.

To give, then, a proper answer to the question, whether in the combustion of petroleum or of stearin an increase or diminution of weight occurs, care must be taken that the gases formed do not escape into the air, but are held fast. This is effected by means of a white substance which is sold under the name of caustic soda, and is cast into rods or broken into irregular pieces. With this substance the upper part of a lamp cylinder is loosely filled, a piece of wire being fixed into the cylinder preventing the caustic soda from falling down. The cylinder is then placed on the balance in such a way that a small lamp or a candle can be placed underneath it (Fig. 9).

When the whole has been brought into equipoise the lamp is lit. In a short time that side of the balance on which the lamp is, sinks, thus proving that the petroleum and the stearin on combustion are converted into substances which are heavier than the part of the combustible substance which disappears.
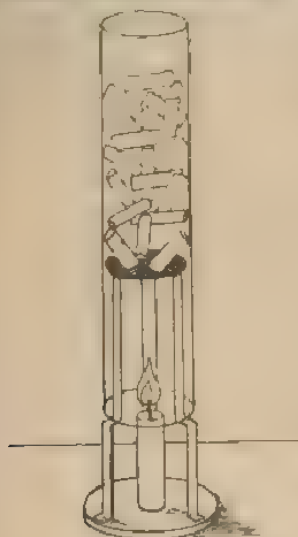
From these experiments we can draw the general conclusion that combustion consists in the chemical action of the combustible substances on some other substance which combines with them to form new substances. For, according to the law of the conservation of weight, the increase of weight can be produced only by the addition of another ponderable substance to the substances undergoing combustion.

This substance will be sought for in the air, since, in the case of the processes we are considering, there is no possibility of the access of any other ponderable substance.

Fig. 9.

34. Behaviour of the Air during Combustion.— For the purpose of getting a more exact knowledge of the process of combustion in this direction, we must shut it off from the rest of the outside world in such a way that we can investigate all the changes which occur in the participating substances. We therefore carry out the combustion in a closed space, in a glass flask.

The first thing that we notice here is, that in a given volume of air it is not possible to burn any quantity of oil, but that the amount burned is greater, the greater the volume of the air. There is, therefore, something contained in the air which is necessary for combustion.

The air, however, does not consist entirely of this something. No matter what substances are burned in a given quantity of air, one never succeeds in using up the whole amount of air; on the contrary, about ⅘ths of it remain behind. In this residue, combustion can no longer be produced, and closer investigation shows that the gas remaining has other properties than the air. From this it may be concluded that the air is not a simple substance, but a mixture (a solution), consisting of a substance which is necessary for combustion, and of another which does not effect combustion.

35. Oxygen.—That the power of the air to support combustion depends on the presence of a gaseous substance which does not constitute the whole air, but only about ⅕th of it, was stated by the chemist Scheele (born at Stralsund), towards the end of the eighteenth

...cury. Scheele confirmed his opinion, which was opposed to the ...en existing ideas of the "elementary" nature of the air, by showing how to prepare a substance which had the power of supporting combustion in a much higher degree than ordinary air, and which left ... and so residue incapable of supporting combustion.

Scheele obtained his gas, which he called *fire-air*, by strongly heating the substance well known by the name of *saltpetre*. He afterwards obtained it in the same manner from the mineral *pyrolusite*.

Independently of Scheele, the same substance was discovered
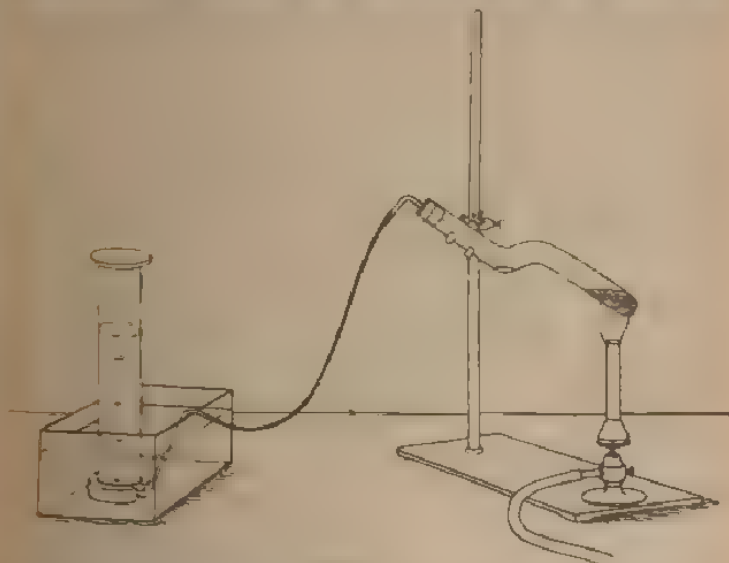
FIG. 19.

...what later by Priestley, who prepared it by strongly heating a ...low substance called *oxide of mercury*.

The last experiment is the most convenient for repetition. The ...yellow powder (oxide of mercury) is placed in a bent tube of hard ...lass (Fig. 19). The tube is closed by a perforated cork, carrying a ...ass tube with indiarubber tubing attached. On heating the tube ...ning the oxide of mercury, this substance first becomes darker, ...black, in colour. After some time a film with a metallic lustre ...formed on the tube near the heated part. If the end of the gas-...ery tube is placed under water, bubbles of gas are seen to rise. ...might be taken for air, which is caused to expand by the heating, ...usually escapes from the tube. We can readily convince our-...however, that the gas is not ordinary air; for if a splinter of ...wood which has been lit and then blown out, so that only the charred ...glows feebly, be brought to the mouth of the tube, it at once

II. Metals

F. Alakali metals. \
G. Alkaline earth metals. — Light metals. \
H. Earth metals. \
I. The iron group. \
J. The copper group. — Heavy metals. \
K. Other metals.

The above grouping is by no means ideal, still it has the ad tage of bringing together the most important natural groups of elements.

The two divisions of the metals, the light and the heavy, so formed that the first division contains the metals whose des does not exceed 4, while to the second division belong the metals higher density. With this apparently rather external and arbit distinction, there are bound up important chemical differences, w form the real justification of the division.

We pass now to the characterisation of the individual elements

Non-Metals

A. Hydrogen and the Halogens

Hydrogen is a colourless gas which is more difficult to bring the liquid and solid state than any other substance except helium. is the lightest of all known substances, for 1 cc. of it weighs ne "normal" conditions, *i.e.* at 0 C. and under a pressure of 76 mercury, only 0 000090 gm. It does not occur in appreciable quan in the free state in nature, although there is probably a very sm quantity of it present in the air.

In compounds, hydrogen is met with very frequently. Wa which covers $\frac{3}{4}$ths of the earth's surface, is a compound of hydro with oxygen. Moreover, hydrogen is present in almost all substances of which the bodies of animals and plants are built up.

Fluorine is a faintly yellowish-green coloured gas which does occur in nature, and which can be prepared only with difficulty, si it at once interacts chemically with almost all substances.

Its naturally-occurring compounds are not rare; the best known fluor-spar.

Chlorine, likewise, does not occur free in nature, and must prepared from its compounds. It is a yellow-green coloured g with a powerful smell, and has a very harmful action on life of kinds By moderate pressure, it can be condensed to a yellow gre coloured, oily liquid, which is prepared on a manufacturing scale a sold in metal bottles. Chlorine, also, has the power of readily formi chemical compounds.

Compounds of chlorine occur widely in nature. The most important and best known is *common salt*, the familiar white substance, which is soluble in water and which we are wont to add to almost all our food. *Hydrochloric acid* is a compound of chlorine and hydrogen.

Bromine is a dark brown-red liquid, transparent only in quite thin drops, and is one of the few elements which are liquid at ordinary temperatures. Even at room temperature, it passes very readily into a yellow-red, heavy vapour which has an exceedingly disagreeable smell, and has a caustic action on all organisms. It shares with iodine and chlorine the widely extended combining power, but possesses this to a less degree than those elements. Bromine does not occur free in nature.

The best known compound of bromine is *potassium bromide*, a white salt readily soluble in water, which finds application in medicine and in photography. The bromine compounds occur, indeed, widely distributed in nature, but generally in small quantities, so that bromine belongs to the somewhat rarer elements.

Iodine is a solid, crystalline substance of a blackish-violet colour, with a lustre which approaches that of the metals. It volatilises even at room temperature, sufficient, however, for it to have a marked and not pleasant smell. At higher temperatures it melts and passes into a vapour of a fine violet colour.

Iodine dissolves in various liquids, giving solutions which are sometimes coloured brown, sometimes violet. A solution of iodine in alcohol, employed in medicine under the name of tincture of iodine, is a brown liquid having the smell of its two components.

Iodine does not occur free in nature; its compounds are sparsely distributed. *Potassium iodide*, a white salt readily becoming yellow when coloured owing to the separation of iodine, finds frequent application.

B. THE OXYGEN GROUP

Oxygen is a gas which forms a constituent of the atmospheric air we breathe, and as such is exceedingly important for living nature. The source of energy which the organisms require for the exercise of their functions is derived from the combination of the substances of which they consist with oxygen. Likewise, all phenomena of combustion by means of which we warm our houses and drive our engines depend on the co-operation of oxygen.

Oxygen gas is, in thin layers, colourless; in very thick ones, blue. By strong cooling it can be condensed to a bluish liquid which boils at 180 C.

Besides the large quantities of oxygen which occur free in the air there are also enormous quantities of the element contained in compounds. Most of the compound substances which we find at

the earth's surface contain oxygen. Of these compounds, the most important is water (cf. p. 46). In weight, oxygen far surpasses all other elements at the earth's surface.

On account of the great importance of oxygen and of its compounds for all life, and on account of the very numerous compounds which it forms, this element occupies a specially prominent place in chemistry, and may be designated as the most important of all the elements.

Sulphur is a well-known, yellow, solid substance which melts at 120° C. to a honey-coloured liquid and readily inflames in the air. It burns with a blue flame, forming a gaseous oxygen compound which is easily recognised by its pungent odour.

Sulphur does not conduct electricity, and readily becomes negatively electrified on being rubbed.

Sulphur is widely distributed in nature. It occurs in large quantities, especially in volcanic regions, sometimes pure, sometimes impure through admixture with earthy matter. Not inconsiderable quantities of sulphur are also found in places where a decomposition of salts containing sulphur is effected by peat or brown coal.

Sulphur is met with in much larger quantity in chemical compounds than in the free state. *Gypsum* and *iron pyrites* may be mentioned as the best known of these substances.

Besides the oxygen compound of sulphur just mentioned, a hydrogen compound forces itself on the observation through its conspicuous and unpleasant smell. This substance is produced in the decomposition of many animal substances, *e.g.* eggs, and the "smell of rotten eggs" thereby produced is in reality the smell of this compound, sulphuretted hydrogen.

Selenium and *Tellurium* are two very rare elements whose compounds are similar to those of sulphur, whereas the free elements differ in their properties. Selenium is generally a black red, solid substance which does not conduct electricity. Besides this, however, another form of selenium is known which has a half-metallic lustre and a slight electrical conductivity. In nature, selenium occurs almost entirely in the form of compounds; occasionally, it is found in traces accompanying sulphur.

Tellurium is a grey, solid substance with metallic lustre, and conducts electricity like a metal. It, also, occurs in nature generally in compounds.

C. THE NITROGEN GROUP

Nitrogen is a gaseous element occurring, to a preponderating extent, in the free state; the amount of the nitrogen compounds in nature is small compared with that of elementary nitrogen. It forms the chief constituent of atmospheric air, which is a mixture (not a

chemical compound) of 4/5ths nitrogen and 1/5th oxygen by volume. As can be understood from the known properties of the air, nitrogen is colourless, odourless, and tasteless. By great cold it, also, can be condensed to a liquid ; with greater difficulty, however, than oxygen. Its boiling point lies lower than that of oxygen, viz. — 194° C.

Although the nitrogen compounds are, in amount, inferior to the free nitrogen, they are, nevertheless, of very great importance, since the most important constituents of the vegetable and animal structures are nitrogen compounds. Especially the substance of the *muscles* and the contents of the cells, the so-called *protoplasm*, to which the real life activity is attached, are nitrogenous.

Of the better known compounds of nitrogen in the mineral kingdom, *saltpetre* and *sal ammoniac* may be mentioned.

In contradistinction to the elements we have hitherto mentioned, elementary nitrogen possesses only in a very slight degree the power of interacting chemically with other substances. It is, therefore, characterised as a chemically inert or indifferent element. To obtain nitrogen compounds one cannot, therefore, as a rule, start from nitrogen itself, but the desired substance must be prepared from other nitrogen compounds.

Phosphorus is an element which is classed along with nitrogen, not on account of their similarity in the elementary state, but because of the similarity of the corresponding compounds. The free elements themselves are widely different.

Phosphorus is known in two different forms, which possess quite different properties, but represent chemically, both of them, elementary phosphorus. This is seen from the fact that both forms, in their reaction with other substances, always give the same compounds in the same proportions, and each can be converted into the other without loss. The difference between them must be interpreted in somewhat the same way as the difference between water and ice, only that in the case of phosphorus the transformation does not take place so easily.

The first form of phosphorus is a semi-transparent, faintly yellowish substance which has the property of appearing luminous in moist air ; whereby it evolves fumes and changes into an acid liquid. This is due to the fact that phosphorus, even at the ordinary temperature, combines with oxygen ; it undergoes slow combustion. At a somewhat higher temperature, the slow combustion passes into rapid combustion, when the phosphorus burns with a bright, yellowish-white flame, with formation of white fumes.

The second form of phosphorus appears as a black-red powder which neither fumes nor appears luminous in the air, nor becomes oxidised. This *red phosphorus*, also, takes fire much less easily than the first mentioned *white phosphorus* ; having once taken fire, however, it burns in the same way as the white form.

Each variety can be transformed into the other by the action of

heat.   The relations which are here met with will be discussed
(Chap. XV.)

Only compounds of phosphorus occur in nature.   These also
an important part in living nature.   The bones of the verte
animals contain compounds of phosphorus, and serve as the sta
point for obtaining the element.

Arsenic, in its compounds, is closely allied to phosphorus, and i
free state, also, has a certain similarity to it.   It is a black suba
with a feeble metallic lustre, and conducts electricity like a m
On being heated, it passes into a vapour without previously mel
the vapour, likewise, on cooling, passes directly into solid arsenic.

In nature, arsenic occurs both in the elementary state an
compounds, especially with the heavy metals.

The most conspicuous property of arsenic is its great poisonous
All compounds of this element are more or less poisonous.   Mo
the cases of arsenical poisoning occur with an oxygen compoun
this element, which is commonly called *white arsenic* or simply arse
it is a white, almost tasteless powder, slightly soluble in water.

D. THE CARBON GROUP

Carbon, —The peculiarity which was found in the case of son
the preceding elements, that there exist different solid forms w
yield exactly the same transformation products, is present in a
marked degree in the case of carbon, for this element is know
three quite distinct forms.   Ordinary black charcoal, the purest t
of which is *soot* : *graphite*, the material of lead pencils ; and, la
the *diamond*, the colourless, strongly refracting and exceedingly h
precious stone,—all consist of carbon, and yield, in all chemical tr
formations, equal quantities of the same final product.

Besides these forms of elementary carbon, which generally oc
in nature mixed with impurities, there are numerous compounds
derivatives of carbon.   It is present in enormous quantities in
mineral world (in limestone), and forms a never absent constituen
all *organisms*.   The different compounds of carbon occurring in
animal and vegetable kingdoms give rise, in chemical actions,
numerous other compounds.   Above all other elements, carbon
endowed with the greatest power of forming different derivatives,
the number of substances which contain carbon so greatly exceeds
number of the compounds of the other elements that the chemistry
the carbon compounds forms, under the name of *organic chemistry*
special part, and, indeed, as regards the number of known substan
the larger part of all chemistry.

These *organic compounds* consist, in the simplest cases, of carbon a
hydrogen ; to them belongs petroleum, which is a mixture of vari

hydrocarbons of similar composition and properties. Oxygen, in addition, is contained in the substances which are classed together under the name of the *fats*, and also in the starch and sugar-like substances which occur to a specially large extent in plants. The compounds, of which the muscles and the nerves are built up, and in which the chemical processes of life for the greater part take place, contain, besides the already-mentioned elements, nitrogen and generally also sulphur and phosphorus. That carbon is contained in all these substances is readily seen when they are strongly heated. The charring which thereby takes place consists essentially in the other elements escaping as volatile compounds, leaving behind the portion of the carbon which does not disappear with these compounds, as charcoal.

After oxygen, carbon must be designated as the most important element.

Silicon is an element which does not occur in the free state on the earth. In the form of an oxygen compound, known as *silicic acid*, and derivatives of this, silicon is, however, one of the most widely spread elements.

Silicon, like carbon, can be obtained in various forms, as a brown powder, and as an iron-grey brittle mass with metallic lustre. This latter form conducts electricity.

An oxygen compound of silicon, silicic acid, constitutes, as quartz, a large part of the soil and the mountains. Compounds of silicic acid with various metals, especially of the group of light metals, compose most of the rocks. Silicon is, therefore, essentially the element of the crust of the earth.

Boron is an element which does not occur to a large extent in nature. It is never found free, but must be prepared from its compounds. The properties of elementary boron are similar to those of silicon.

The most important compound of boron is likewise that with oxygen. This is contained in *borax*, a salt used in the arts for solder and for some other purposes, and which is the best known of all the compounds of boron.

E. THE ARGON GROUP

In atmospheric air there are found in very small quantities a few gases which have only recently been discovered, and which are distinguished by the peculiarity that none of them has ever been made to enter into chemical combination. They are known, therefore, only in the elementary state.

The longest known is *argon*, which is present in the air to the extent of rather more than 1/100th part by weight, and remains behind when the other components have been converted into stable chemical compounds. It is a colourless gas, which, on account of its inability

to form chemical compounds, is also odourless and tasteless.   Its den
is greater than that of air.

Besides argon, a few other gases of similar chemical indiffere
have been discovered.   These, likewise, occur in the air, but in m
smaller quantity ; they are also contained in measurable quanti
enclosed in some minerals.   They are called *Helium, Neon, Kryp*
and *Xenon*

The Light Metals

F. The Metals of the Alkali Group

The metals of this group have many properties in common.   Th
have a low density, some of them lower than that of water.   Th
power of forming chemical compounds is very highly developed,
that they never occur free in nature, but must first be prepared
energetic means from their compounds.   By reason of their gr
combining power they have the property of reacting chemically w
most other substances, and can, therefore, be preserved only by obse
ing special precautions.

Potassium.—Fresh surfaces of this light metal show a fine sil
lustre.   It readily melts, and is, even at the ordinary temperatu
soft like wax.   At a red heat it passes into vapour.

In nature, only compounds of potassium occur.   As the best know
of these, *saltpetre* and *potashes* may be cited.   The most important
carnallite, which is obtained in large quantities in some parts
Germany, apparently as the residue left on the evaporation of
previously existent sea.   Plants require potassium compounds f
their growth, and where these are not present in sufficient quantity
the soil they are added as manure in the form of carnallite, or of t
compound prepared from it and richer in potassium, *potassium chlori*

Potassium compounds of all kinds play an important part
the arts and manufactures   Potassium is also of importance in t
organism of man and the animals ; it forms an essential component
the red blood corpuscles.

The elements *rubidium* and *caesium* are allied to potassium.   The
properties are almost identical with those of potassium, both
elements and in compounds   In contrast with potassium, howeve
they occur in very small amount in nature.

Sodium is, in its properties, a light metal very similar to potassiu
Its compounds are likewise found in enormous quantities in natu
The best known and most important of these is *common salt* (p. 47
which consists of sodium and chlorine.   It serves as starting-point f
the preparation of most of the other sodium compounds, as also of th
chlorine compounds.   *Soda* and *Glauber's salt* are also compounds
sodium.

Lithium is a rare element, which, in its properties and compounds, agrees least with the other elements of this group. It finds no great application.

G. THE ALKALINE EARTH METALS

The elements of this group share with the alkali metals the property of a low density and of a highly developed combining power. Whereas these, however, cannot be exposed to the air without at once combining with the oxygen, the alkaline earth metals in a dry state remain unchanged in the air. They are also much more tenacious and more difficult to melt and to volatilise than the alkali metals; they have, therefore, more the character of the ordinary metals.

Magnesium is a white metal, somewhat of the colour of tin, which remains unchanged in the air as long as the temperature is low. On being heated it takes fire and burns with a brilliant light, forming an oxygen compound.

Compounds of magnesium occur very largely in nature. Almost all rocks which contain silica acid also contain magnesium in the form of a compound with silicic acid. There are also other minerals which contain magnesium. In daily life several magnesium compounds find application; the most important are *magnesia*, which is an oxygen compound of the metal, and *Epsom salts*.

Metallic magnesium does not occur in nature any more than any of the other light metals.

Calcium is similar to magnesium, but oxidises with much greater readiness. Compounds of this element occur in nature in large quantities, and have an essential share in the building up of the earth's crust.

Of such compounds there should be mentioned *limestone* and *dolomite*; the latter contains magnesium as well as calcium.

Marble, the use of which is known, is a specially pure form of limestone. From limestone mortar is prepared. Gypsum, also, and cement, which find a similar application to mortar, contain calcium. The calcium compounds are largely applied in the manufactures.

Strontium and *barium* are two elements which, in their whole behaviour, are closely allied to calcium. Their compounds, however, occur in much smaller quantity, although they cannot actually be regarded as rare.

Lastly, *beryllium* must be mentioned as an element belonging to this group. It has the same relation to the other members as lithium to the other alkali metals, i.e. it shows less similarity to the other members than these to one another. It is a rare element, deriving its name from its occurrence in the mineral beryl.

H. The Earth Metals

The elements of this group have the character of the ordinary metals in a much more pronounced manner than those of the preceding groups. Of the large number of metals which could be mentioned here, only one, *aluminium*, can claim our attention, since the compounds of the others occur so rarely in nature that they play no important part, either with regard to the composition of the solid crust of the earth, or through application in the arts or in medicine.

Aluminium, which does not occur free in nature, is, in its oxygen compound and derivatives of it, widely distributed, and is, after oxygen and silicon, the third most frequent element in the earth's crust. It is an almost unfailing constituent of the rocks which contain silicic acid. When these undergo mechanical and chemical disintegration under the action of moisture and other atmospheric influences, *clay* separates out, which is a compound containing silicon and aluminium along with oxygen, and which, in different forms, is the chief constituent of the sedimentary or stratified rocks. The technical application of clay to the making of bricks, vessels, and modelled objects of all kinds is also very important.

In recent years the metal aluminium has been prepared in large quantities from its compounds with the aid of the electric current. It is, as is known, a white, light metal which keeps well in dry air but is readily attacked in water, especially in salt water.

The remaining very rare alkaline earth metals we shall not describe here. The best known are *scandium, yttrium, lanthanum, cerium, neodymium, praseodymium, ytterbium.*

The Heavy Metals

I. Metals of the Iron Group

Iron is an element the properties of which, on account of its universal use, are well known. It is a hard, difficultly fusible metal which remains unchanged in perfectly dry air, but in moist air, and under the influence of various substances, very quickly *rusts*, i.e. forms a compound with the oxygen of the air.

The somewhat different properties which iron exhibits as cast iron, wrought iron, and steel, are due to the presence of small amounts of other substances, more especially carbon. The properties of pure iron agree most nearly with those of wrought and ingot iron, which are the purest commercial kinds of iron.

In nature, the occurrence of iron in the elementary state is exceptional; its compounds, however, are universally distributed and occur in large quantities. On the whole, iron occurs less frequently than aluminium, but more frequently than calcium and magnesium.

Although iron compounds are present only in small amount in the animal and vegetable organism, they appear, nevertheless, to play a very important part, since the red blood corpuscles of the vertebrate animals, as well as the green cells of assimilating plants, contain iron.

Allied to iron are the nearly related elements *manganese, cobalt,* and *nickel.* They all belong to the less frequent, although not rare, elements.

Manganese, in the metallic state, greatly resembles iron, only that it rusts still more easily than the latter, thereby becoming coated with a dark brown oxygen compound. In the metallic state it is not much used. Its compound with oxygen, pyrolusite, however, which is employed for the production of a colour for pottery, has a varied and important application in the arts.

Cobalt is, even in moist air, much more resistant than iron and manganese, but finds little application as a metal. Its most remarkable property is that its oxygen compound dissolves in glass with a dark blue colour. It finds application, therefore, for the production of a blue colour, cobalt blue or *smalt*, and also for the colouring of glass and pottery.

Nickel is still less changeable in the air than cobalt and is, therefore, used for making articles intended to resist heat and moisture. Objects made of other metals are also, with the help of the electric current, plated with nickel; these nickel-plated articles preserve the white-like lustre of that metal, since nickel is also fairly hard and tenacious. In this fact lies the importance of this element as regards its applications. Nickel *compounds* are of no great importance.

Nickel mixed with copper and zinc forms *German silver.*

Chromium is a metal very similar to iron, only harder and more brittle, which remains quite unchanged in the air, but is easily attacked by a number of liquids. The pure metal has no application; addition of chromium to steel improves the steel.

In nature it occurs chiefly in the form of an oxygen compound which also contains iron, and is called *chrome ironstone.*

It forms various compounds, of which *chromic acid* and *potassium* ... have a varied application in the arts. The artists' colours chrome yellow and chrome red, are derivatives of chromic acid.

Allied to chromium in their chemical relations are several metallic ... of rare occurrence and possessing no great importance; it ... sufficient at this point to give their names. They are *molybdenum, tungsten, uranium.*

The two metals *zinc* and *cadmium* are, in many respects, related to the metals of the iron group, but show, on the other hand, a certain similarity to magnesium.

Zinc is a well known grey white metal, rather more resistant to air than iron, but inferior to this in difficult fusibility and ... tenacity. As it can be readily rolled to sheets and

soldered, it is applied for all purposes for which a not very t
metal, but one which is fairly resistant to water, can be used in
form.

In nature, zinc occurs only in the form of compounds, of w
that with sulphur, called *zinc blende*, is the most important.

Cadmium is a metal which is very similar to zinc, only softer
more easily fusible, and which occurs in small amount along with
in its naturally occurring compounds or ores. The artists' co
cadmium yellow or, shortly, cadmium, is the sulphur compound of
metal.

J. METALS OF THE COPPER GROUP

The metals here grouped together are distinguished from
preceding ones by a greater resistance to the chemical influence
air and water. This is, certainly, no perfectly universal characteri
for while some of the members of this group belong to the
metals which, under ordinary circumstances, do not change at
others become more or less quickly coated in moist air with layer
oxygen compounds which destroy their metallic lustre The action
however, usually restricted to the surface, so that, after all, a fa
great durability with respect to the destructive chemical influence
present.

Connected directly with this property is the fact that these me
can be more readily obtained from their naturally occurring compou.
or ores, than those previously mentioned, and also that they are of
found in the free state In this and the next group, therefore,
metals first met with in the history of the arts are found, and
metal mentioned in the oldest literary monuments, and usua
rendered in English by " bronze," is a mixture, the chief constitu
of which is copper, the typical element of this group.

Copper is a metal which has been long known, and the rose-
colour of which is found in no other metal. The true colour of cop
is seen only on fresh surfaces, since it quickly tarnishes in the
and becomes covered with a coating of oxygen and sulphur compoun
which, however, is very thin and attains to no great thickness ev
after many years.

Copper is an excellent conductor of electricity and is, therefo
used for all kinds of electric conductors. Its chemical resistibili
combined with its toughness and high melting point, give it a wid
technical applicability.

In nature, metallic copper is not of rare occurrence : of much me
frequent occurrence, however, are its compounds with sulphur a
oxygen.

Of the better-known compounds of copper, *copper vitriol*, a blu
crystalline salt, may be mentioned

Lead is a grey, soft metal of high density and low melting point Its fresh surfaces exhibit a high metallic lustre they tarnish, however, very readily through taking up oxygen from the air The coating remains thin, and the lead, therefore, resists further destruction for a very long time It shows a similar behaviour with respect to many other attacks, so that it is indispensable in chemical manufactories in which corrosive substances are prepared.

On account of its great softness, pure lead is not much used. By mixing it with other metals it can be made harder, without its losing its chemical resistibility It is also used for coating other metals, especially iron

In nature, lead occurs chiefly in the form of a sulphur compound, which is called *galena*, and is the most important lead ore.

Lead compounds are largely used in the arts. *Litharge* is an oxygen compound ; *sugar of lead* a compound with acetic acid.

The lead compounds act on organisms as cumulative poisons, *i e* the effects of small amounts, which singly are not appreciable, are added and ultimately produce very serious symptoms

Closely related to lead in many respects is the rare metal *thallium*, which, in other respects, is allied to the alkali metals.

Mercury is a metal, liquid at ordinary temperatures, which solidifies at — 39° C. and boils at — 357 C. It belongs to the noble metals, since it preserves its bright surface in moist air, *i.e.* it does not combine with the oxygen At a higher temperature, however, combination takes place (p 53)

Being the only metal which is liquid at ordinary temperatures, it is widely employed for physical apparatus, such as thermometers and barometers and for other purposes in technical science Its utility is greatly enhanced by its unchangeableness in air ; its high density, makes it useful for some purposes.

In nature, it occurs in the free state, but chiefly as a sulphur compound This is called *cinnabar* the artists colour of the same name is specially pure sulphide of mercury, which is usually artificially prepared

The soluble mercury compounds act as powerful poisons they find application in medicine

Silver is a white metal which is not affected by oxygen The black stains which silver objects sometimes exhibit is due to the formation of a sulphur compound through the action of air containing it, or of other sulphurous substances

The property of its compared with pure or native silver being to be obtained very easily and, on this and on its unchangeableness in air make it a very good ... metal as a metal for coinage

... silver occurs partly in the metallic state and partly as ...

comparatively high temperatures.   This view would, however, n
quite a correct one.   On making the appropriate investigatio
temperature can be found at which combustion just begins, and
that below this point no combustion takes place at all.   On the
trary, we are dealing here with a gradual transition.

Combustible substances, therefore, combine with oxygen
temperatures, but *with very different velocities*.   The higher the tem
ture, the more rapid is the combination ; on the other hand, a
temperature falls, the process becomes slower and soon diminish
as to be inappreciable.

 * 54. **Slow Combustion.**—A body can, accordingly, beg
combine with oxygen at certain medium temperatures, without ta
fire.   Ignition occurs only when the heat developed in the combt
raises the adjacent portions of the body to such a high temper
that these also burn with sufficient rapidity.   The temperature
these adjacent parts attain, depends, on the one hand, on the am
of heat conveyed to them by the combustion, and, on the other l
on the amount of heat which they lose by conduction and radia
Not until the former exceeds the latter to such an extent tha
temperature of rapid combination is attained, can this rapid combu
take place.   From this it follows that ignition or the initiatio
an independent combustion, depends quite as much on the form
distribution of the substances as on their nature, as our every
experience with regard to the ignition of combustible substt
teaches us.

55. **Influence of Temperature on the Velocity.** —The
that the velocity of chemical processes, *i.e.* the ratio of the am
transformed to the time required, rapidly increases with rising tem
ture, is quite universal, and is valid for chemical processes of all k
We have, further, no ground for supposing that any chemical pr
which takes place at a higher temperature, cannot take place at a l
If we do not note any transformation, it may be because it takes
too slowly for our observation.

The stock of coal in the cellar burns while it is stored in the c
just as when it is in the fire ; only, in the former case, with so
slowness that we can detect no difference even after several years.
large quantities of coal, however, are stored under such condit
that the dissipation of the heat developed in the slow combustio
prevented, the temperature rises, the process is accelerated, and
become so rapid that it passes into vigorous combustion.
phenomenon is called the *spontaneous ignition* of coal.

56. **Physical Properties of Oxygen** —To determine the de
of oxygen, one must determine the weight of a given amount and
volume occupied by it (p. 27).   The latter can be easily done
glass tube graduated in cubic centimetres.   The weight is less ea
determine, as oxygen is very light, and the determination of its we

to the large vessels necessary causes difficulties. We adopt, therefore, an indirect method.

Potassium chlorate, as we know, evolves oxygen on being heated. In the vessel, a white substance remains behind; a further substance is not produced. If, therefore, the weight of the potassium chlorate taken for the experiment be determined, and, afterwards, the weight of the residue, the difference is equal to the weight of the oxygen evolved. If this is collected in a suitable measuring vessel (Fig. 12), its volume can be read off and its density calculated by the formula _____. If the experiment is performed with 1 gm. of potassium chlorate, it is found that after complete decomposition, the oxygen evolved, on cooling down to room temperature, occupies, in round
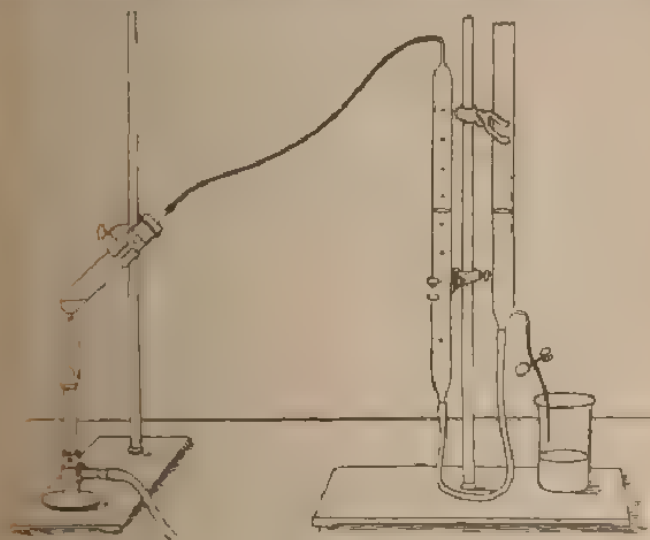
FIG. 12.

numbers, 290 cc. The loss of weight of the potassium chlorate amounts to 0.392 gm., and the density of oxygen is, therefore, 0.00135.

Normal Temperature and Normal Pressure.—This re_____, however, not yet defined with sufficient exactness. The _____ occupied by a gas depends, in large measure, on the pressure _____ temperature, and values for the density, varying within wide _____ will, therefore, be obtained when the determination is per_____ under different conditions. An agreement has, therefore, been _____ to with regard to a *normal temperature* and a *normal pressure*, at _____ the densities of gases shall be determined. As normal tempera-

ture the melting point of ice is taken, on the centigrade thermom
this point is marked 0.[1]

As normal pressure there has been adopted the *mean atmos*
pressure, which is taken equal to the pressure of a column of mer
76 cm. high.

Since, however, the density of mercury is also dependent on
temperature, we must add that the temperature of the mercury
be 0 C. The density of mercury is then equal to 13·595 ; 1 cc. we
therefore, 13·595 gm., and a column of 1 sq. cm. section and 76
high weighs $76 \times 13 \cdot 595 = 1033 \cdot 2$ gm.

The pressure of one atmosphere is, therefore, equal in effect
weight of 1033 gm., or rather more than 1 kilogm., on an are
1 sq. cm.[2]

58. **Boyle's Law.**—The volume occupied by oxygen gas cann
always determined at 0 C. and u
atmospheric pressure, and the d
mination made under other condi
must be appropriately reduced.
this purpose, a knowledge of
behaviour of oxygen to change
pressure and *temperature* is necessa
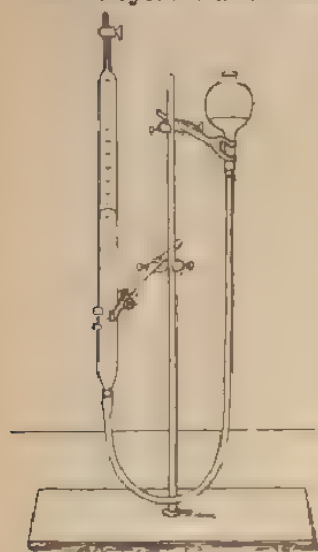
A knowledge of the first is
tained by means of the appar
shown in Fig. 13. The oxyge
contained in a graduated tube,
lower end of which passes into
indiarubber tube ; to the other
of this a movable vessel is atta
Part of the measuring tube,
indiarubber tube, and the v
are filled with mercury. The p
ure under which the oxygen st
can be altered by raising and lowe
the vessel. The volume occu
by the oxygen can be read off

FIG. 13.

the graduated tube. The pressure in cm. of mercury is the

[1] In Great Britain, for the purposes of daily life, thermometers with the Fahr
scale are used. On this scale the melting point of ice is marked 32. One degr
the Fahr. heat scale is equal to 5/9ths of a degree on the centigrade scale. Tr.

[2] Since the weight of a given mass varies somewhat with the locality, the u
pressure defined above is also subject to the same variation. In cases of greater
ness it is assumed that the weight determination is made at sea level and in the lat
of 45, or, that the determination, when made elsewhere, is recalculated to these
ditions.

The adoption of *absolute units* is still better. Since the force with which 1 gram
in consequence of gravitation, is, at sea level and in latitude 45, equal to 9
absolute units (p. 24) it follows that the pressure of the atmosphere is equ
$980 \cdot 6 \times 1033 \cdot 2 = 1,013,140$, or very nearly 10^6 absolute units. A column of mercu
(instead of 76) cm. high would give, almost exactly, 10^6 absolute units of pressure.

the external atmospheric pressure (height of the barometer) and the difference of level of the two surfaces of mercury. This difference of ... to be reckoned with negative sign when the outer mercury surface ... lower than that which bounds the oxygen A number of corresponding values of volume and pressure are in this way determined.

By means of such measurements, which have been carried out by various physicists with great care, it has been found that a very simple relation exists between pressure and volume. Denoting any two pressures by p_1 and p_2, and the corresponding volumes of oxygen by ... and v_2, the formula holds, $p_1 : p_2 = v_2 : v_1$, or, $p_1 v_1 = p_2 v_2$. The pressures are, therefore, inversely proportional to the volumes, or *the products of all corresponding values of pressure and volume are equal.*

The ... found here for oxygen gas is not peculiar to this substance, but ... for all other gases. It was discovered in 1660 by Boyle, and is called after him.

The Law of Gay-Lussac and Dalton.—Pressure is not the only circumstance which influences the volume of a gas The ... changes also with the *temperature*, increasing and diminishing ... the same sense as the temperature rises and falls. To determine ... amount of this change it is necessary to choose another fixed ... besides that of melting ice The temperature of boiling ..., and, since this changes with the pressure, the temperature of ... boiling under a pressure of one atmosphere ($= 76$ cm. mercury) ... as such a temperature.

To obtain the amount of the change of volume between these two ... we use the same apparatus as was employed in demonstrating Boyle's law (Fig 14). The graduated tube containing the ... is surrounded with a glass mantle in which are placed ... and pieces of ice. The oxygen soon assumes the ... of melting ice, and, after the outer vessel has ... so placed that the two mercury surfaces stand at an ... height, the volume occupied by the oxygen at 0 C. and ... the then existing atmospheric pressure, can be read off The ice is then removed, and in its place steam is passed ... the mantle The volume of the oxygen increases, ... again brought the two mercury surfaces to the ... height, we can read off the volume which the oxygen ... under the same pressure as before, and at the ... of boiling water. Exact measurements of the ... change show that the volume has increased in ... 1 367.

... has also proved to be a universal law valid for ... The number obtained is, therefore, the expression ... special property of oxygen but of a *universal property* ... The law, that all gases expand by the same ... between corresponding temperatures, was discovered simultane-

ously by Dalton and Gay-Lussac in the year 1801; it is generally ca[
after the latter.   In symbols, the law can be formulated thus :—

$$v_t = (1 + at)v_m$$

where v_t is the volume at the temperature t, v_m that at the melt
point of ice, and a the hundredth part of the expansion between
melting point of ice (0° C.) and the boiling point of water (100°
In numbers, $a = 0.00367$ or $1/273$.

This formula gives the expansion starting from the temperatur[
melting ice.   To obtain the expansion between any two temperatu
t and t', the above formula is applied to both temperatures, and
eliminated from the two equations.   There is obtained

$$\frac{v_t}{1 + at} = \frac{v_{t'}}{1 + at'} = v_0.$$

From this it is seen that the volume observed at temperature t
reduced to the volume at normal temperature, 0° C., by dividing it
the quantity $1 + at$.

* It must be specially emphasised that the quantity a is
hundredth part of the expansion of unit volume between the melt
point of ice and the boiling point of water, and not, let us
between any one temperature and another 100° C. higher.   As
easily be seen, the value of a, the *coefficient of expansion of gases*, wo[
be dependent on the choice of the initial temperature.

60. **The Temperature Scale.**—Since the expansion by heat
the same value for all gases, independently of their nature, the cha[
of volume of gases is used for temperature divisions.   The tempe
ture of melting ice is called zero, and that of water boiling un[
atmospheric pressure 100.   This range of temperature is divided i[
a hundred parts or *degrees*, which are assumed proportional to [
change of volume   To distinguish this graduation from others wh[
are also used, it is called the centigrade or the Celsius scale, and
denoted by C.

Let, then, the volume of a given quantity of oxygen or of anoth[
gas contained in a tube, be denoted by 0° C. (Fig. 15), the volume
the boiling point of water will be defined by the spot marked 100°
and the volumes oc and os will be to one another as $1 : 1.367$.   T[
length cs is divided into one hundred parts, and each of these p[
denotes 1° C.   Such a tube, in which the gas is enclosed by means of
easy moving piston, and which is graduated in the manner just describ[
could, evidently, be used as a *thermometer* or measurer of temperatu[

61. **The Absolute Zero.** The temperatures, however, which a[
met with, are not confined to the range between the melting point[
ice and the boiling point.   Beyond the latter, we can, evident[
extend our thermometers indefinitely, for there is no evidence of
limit for higher temperatures.

Towards the other side, however, our thermometer is limited, for we can subtract only a definite number of degrees before reaching the zero point of volume. This number can be calculated as follows. If we take the volume or 1, the volume is 0 367; one degree is the hundredth part of this; its volume, therefore, amounts to 0 00367, and we can subtract, in the direction of o, only as many degrees as the number of times this fraction is contained in the unit. Now, 00367 273; if we could lower the temperature 273 below the melting point, the oxygen or any other gas must occupy the volume zero.

Apart from the fact that all gases liquefy before this condition is reached such a low temperature has, as a matter of fact, never been produced the lowest point which has been reached lies at 260 below the melting point of ice, and the increasing difficulties of descending lower make it quite improbable that the point - 273 will ever be reached. This point is called the *absolute zero*.

The Absolute Temperature —The designation of the temperature of melting ice by 0 C. results in the temperatures below as having negative values. This is not only arbitrary but, in a certain sense, inconsistent, since different temperatures never have the relation to one another of positive and negative magnitudes in the mathematical sense. In science, therefore, another method of reckoning the temperature has come into use. As zero there is taken that unattainable temperature 273 C below the melting point of ice, and the temperature is counted from that point upwards, with the same degree divisions as in the centigrade scale.

Besides the gain of entirely avoiding negative temperature numbers, there is the further advantage that with this method of reckoning, the law of expansion of gases assumes an especially simple form, *its volume becomes simply proportional to the temperature.* If the volume or of our gas thermometer (Fig. 15) is divided into 273 parts, and if this graduation is continued upwards to any extent, the volume measured in these units gives directly the numerical value of the temperature. The temperature measured in this manner is called the *absolute temperature*, in contradistinction to the *centigrade* temperature reckoned from the melting point of ice. The relation between the two scales is very simple, for the absolute degrees amount to 273 units more than the centigrade degrees. If the former are denoted by T and the latter by t, we have the relation

$$T \quad 273 - t,$$
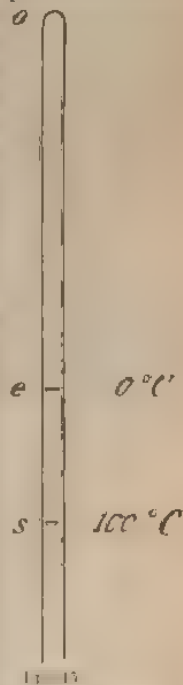
into contact with the gas. We repeat the experiment with the gas obtained from potassium chlorate and observe the same phenomenon A glowing wood-chip is a *reagent* for oxygen, and the *reaction* consists in its inflaming.

49 **Explanation of the Oxygen Reaction.**—Since the combustion of wood in air takes place at the cost of the oxygen therein contained, the question must be asked why the phenomenon has such an essentially different aspect in pure oxygen from that in air. The answer is as follows:—

When the wood burns, a certain amount of heat is produced, which serves to *heat* the gaseous products of combustion, and the higher the temperature thereby rises, the brighter will be the light emitted and the more rapid will be the combustion. When, now, the combustion takes place in *air*, not only must the products of combustion be raised in temperature by the heat produced, but also the *nitrogen* which is contained along with the oxygen, in four times its amount, in the air. On account of the much greater amount of substance to be heated, the temperature does not rise so high in the case of combustions in air as in pure oxygen, and, therefore, the phenomena of combustion are much less energetic.

This result of our consideration, obtained deductively (p. 40), can be tested by mixing pure oxygen with other gases which neither burn nor support combustion; as a matter of fact, the vigorousness of the combustion becomes less in such a mixture, and if the proportion of oxygen in it is very small, no combustion at all can be brought about in it.

50. **Combustion of other Substances.** It follows from the explanation just given that other substances also, which burn in air, will exhibit the phenomena of combustion much more vigorously in oxygen. And still further, one must expect that substances can exist which cannot be made to burn vigorously in air, because the requisite temperature is not reached, but which can burn vigorously in oxygen. Experience confirms both conclusions.

The first phenomenon is seen in the case of sulphur and phosphorus. Sulphur burns in air with a pale blue flame, scarcely visible in daylight. If, however, the burning sulphur be introduced on a long-stemmed iron spoon into a bottle of oxygen, it flares up vigorously and rapidly burns with a bright blue flame.

The difference is seen still more clearly with phosphorus. A piece of phosphorus placed in a similar spoon and ignited, burns in the air with a yellowish-white flame, similar to that of a candle. If the spoon be lowered into oxygen, the bottle forthwith becomes filled with a sun-bright light

51 **Combustion of Iron.**— A substance which cannot be easily made to burn in air, is *iron*. When a piece of iron, a watch-spring for example, is heated in air, it certainly combines with the oxygen, and

the compound produced coats the iron as a grey, brittle mass which breaks off on bending the iron It does not, however, continue burning, and it is only when small particles of iron are scattered in the flame that they can be heated so as to burn entirely (p. 34).

The combustion of iron in oxygen, however, takes place much more readily. A thin steel watch-spring, to the end of which is attached a piece of touch-wood or tinder, can be burned in oxygen like wood. First, the glowing tinder bursts into a vigorous flame, whereby the end of the watch-spring becomes white-hot; then the iron begins to burn with scintillations, and the product of combustion falls down from time to time in the form of a white-hot slag To prevent this cracking the glass, it is well to fill the bottle one-third full with water.

52. **Oxides**. —Almost all the chemical elements are capable of entering into combination with oxygen, and of forming new substances with corresponding increase of weight. From the Greek name for oxygen, *oxygenium*, its compounds with other elements (and also with some compound substances) are called *oxides*. Thus, oxide of mercury is, as we have already learned, a compound of mercury with oxygen. In nature, oxygen and its compounds have a very large distribution. From its occurrence in atmospheric air, which surrounds the whole surface of our earth and penetrates into all its interstices, it follows that those substances which can form compounds with oxygen at the ordinary temperature, must have done so to a large extent in the course of the centuries. This is one of the causes of the wide distribution of oxygen compounds in nature.

53. **The Existence of Combustible Substances**. —Combustible substances, i.e substances capable of combining with oxygen, are, nevertheless, present in large amount in nature in the unburnt condition, and the question arises, why these have not been burnt up long ago. Thus a piece of charcoal or of sulphur can lie exposed to the air for years, or indeed for centuries, without apparently undergoing combustion. That this may take place, the sulphur must be *ignited*, and we have to ask what fresh circumstance is thereby introduced.

Igniting consists in heating one spot of the combustible body to a comparatively high temperature (somewhere about 500 to 600°) It is quite indifferent in what manner the heating is effected; the temperature and contact with oxygen are alone of importance. The heated part then begins to *burn*. An amount of heat is thereby set free by which the adjacent parts of the combustible substance, in their turn, are heated. Combustion passes over to these parts, and so the process goes on till all is burned.

The only respect in which the burning portions are distinguished from those which are not burning is in their *temperature*. It seems as if most substances had the power of combining with oxygen only at

F

the three variables are chosen as the magnitudes to be arbitrarily fixed.

This relation is expressed by saying, *the gaseous state has two degrees of freedom.*

For understanding the behaviour of different systems, a knowledge of their degrees of freedom is a matter of fundamental importance, and this is true not only for the physical, but also for the chemical behaviour. Much use will, therefore, be made later of the conception of the *degrees of freedom of a system.*

* 66. **Geometrical Representation of the Gas Laws.**—It will be recalled that in Mathematics the fact of the mutual dependence of two variable magnitudes, of such a kind that, one of them being given the other must assume a definite value, was expressed by saying that the one is a *function* of the other. In Boyle's law

$$pv = C,$$

where p is the pressure, v the volume of a gas, and C a constant, p is a function of v. Conversely, v is a function of p, for this relation is, necessarily, always mutual.

As can be seen from this example, the content of a quantitative law of nature can be expressed by saying that it represents two (or several) measurable properties of a system as functions of one another.

When the function is given in the form of an algebraic equation there can be calculated for each value of the one variable the corresponding value of the other, and when such calculations have to be frequently performed, a table of the required extent can, once for all, be drawn up. In many cases, however, especially in the investigation of new relations, an algebraic expression for a really existing dependence is not known. In such cases it is important to possess a method which allows of showing clearly the connection between the magnitudes, so that the general relations can be judged. For this purpose the representation by means of *co-ordinates* is generally used in the experimental sciences.

Let it have been found by measurement that to a definite value v_1 of the one variable, there corresponds a value v_1 of the other. On a horizontal line (Fig. 16), starting from a point which has been as origin, one measures off, towards the right a distance of v_1, i.e. a distance which contains as many of the suitably chosen units of length as the amount of the numerical value of v_1. From the point x_1 the value of v_1, also in suitable units, is measured in a perpendicular direction. The point y_1 so obtained is then a representation of the quantitative relations of the two values. This process is repeated for a second pair of corresponding values $x_2 y_2$, and a second point is thus obtained. By continuing the process, a number of such points is obtained, and if an unbroken line be now drawn through all these, a clear picture of the

relation between the two variable magnitudes of the phenomenon under investigation is obtained. The horizontal lengths are called the *abscissae*, and the vertical ones the *ordinates* of the points inserted ; both together are designated as the *co-ordinates*.

The method of representation employed permits also of the representation of negative magnitudes, if the rule be laid down that these shall be reckoned towards the left and downwards from zero, while the positive magnitudes are reckoned towards the right and upwards.

* 67 **The Law of Expansion.**—In illustration, let us apply the method, in the first place, to known laws of nature ; the curves thereby obtained will be a representation of these functions. As a first example we may take the law for the *expansion of gases by heat*,
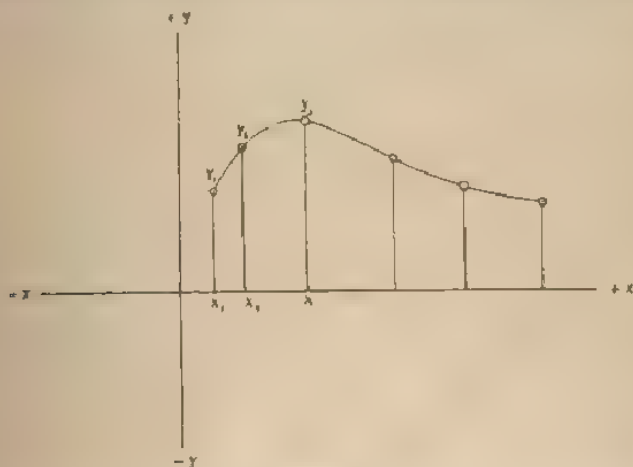
Fig. 16.

the temperatures being regarded as the abscissae, the vo'   s as the ordinates. First of all one calculates the volumes r, corr   ding to different values of t, according to the formula for cons'   ure

$$r   t_0(1 + 0.00995$$

assuming any defini'
obtains a table such

1.037
1.078
1.181
1.467

If w'   of t as abscissae, those of r as ordina
followin   aced (Fig. 17).

doubtful nature of its results in mind. In the present case the supposition would be wrong, since all gases already change their physical state in the known ranges of temperature above the absolute zero, and become liquid or solid

*68. **Representation of Boyle's Law**.—The relation between the volume and pressure of a gas at constant temperature is represented by the formula $pv = C$, where C is a magnitude which varies with the amount of the gas and with the temperature, but for given values of these remains constant. The expression is, evidently, not one of the first degree with respect to p and v, since it contains a
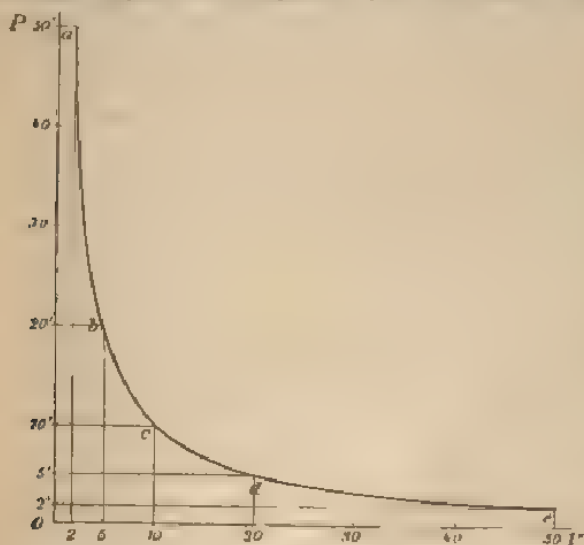
FIG. 18.

product of the two, but is of the second degree. Accordingly, it will not be represented by a straight line. Assuming the constant $C = 100$, one obtains the following table :—

p	
1	100
5	20
10	10
20	5
100	1

The geometrical representation gives the curved line of Fig. 18, which is called a *rectangular hyperbola*. The two branches approach the axes more and more, without ever touching or cutting them. Straight lines which possess this property with relation to a curve, are called *asymptotes*; and the manner of approach is called *asymptotic*. Since, simultaneously with the approach to the one axis, the curve

becomes more and more distant from the other, this relation is
expression of the fact that the volume of the gas never becomes a
however great the pressure, and, likewise, the pressure never beco
zero, however great the volume. However, the extension of
conclusion indefinitely would again be an extrapolation (p. 76),
which the corresponding dubiety would attach.

69. **Density of Oxygen.** After these long but necessary
liminaries, we can calculate, from the observed volume v of
oxygen at the temperature t and under the pressure p, its "redu
volume" v_0 at $0°$ and under the pressure p_v (equal to the pressure
one atmosphere or 76 cm. mercury), by means of the formula

$$v_0 = \frac{pv}{p_v(1 + at)} = \frac{pv}{76(1 + 0.00367t)}$$

According to the very exact measurements of Morley, the weigh
1 cc. of oxygen under normal conditions, amounts to 0.0014290 g
its density is, therefore, 0.0014290. Conversely, 1 gm. of oxy
occupies, under normal conditions, 699.8 cc.; its extensity is, th
fore, 699.8. At any other pressure p and temperature t, these val
are—

$$\text{Density}: 0.0014290 \frac{p}{76(1 + 0.00367t)}$$

$$\text{Extensity}: 699.8 \frac{76(1 + 0.00367t)}{p}.$$

70. **Liquid Oxygen.**—For a long time oxygen was known o
in the gaseous state; it was only in 1877 that Pictet and Caille
simultaneously and independently, converted it into a liquid. T
has a bluish colour and boils, under atmospheric pressure, at   180°
On increasing the pressure, the boiling point rises. In this way,
increasing the pressure to 50 atmospheres, the boiling point can be rai
to   118. At a higher pressure, the phenomenon of boiling c
not be brought about at all; on the other hand, above   118 oxyg
cannot be liquefied by any pressure, however great. These extre
values at which gas and liquid can exist side by side, are called
critical values; 50 atmospheres is, therefore, the critical pressure, a
118 C. or 155 A. the critical temperature, of oxygen. More ex
information regarding the behaviour of substances in the neighbo
hood of the critical point will be given later (Chap. XVI.).

Whereas formerly, liquid oxygen could be obtained only in sm
quantity after laborious preparation, C. Linde perfected a method,
1896, by means of which oxygen could be converted into the liq
state by a continuous process. The method depends on the fact th
strongly compressed air undergoes cooling on expansion. The c

thus produced is then employed to cool down a further quantity of
compressed air, so that when this expands a considerably lower
temperature is produced ; by repeating this cycle uninterruptedly,
the temperature can soon be lowered so far that the expanded air
becomes liquid.

From the mixture of oxygen and nitrogen thus obtained, nitrogen
evaporates off first, since its boiling point lies at - 194 , much lower,
therefore, than that of oxygen ; a mixture is left behind which becomes
increasingly rich in oxygen, and, at last, is almost pure liquid oxygen.

The production of liquid oxygen has, on this account, become so
cheap that attempts have been made to employ it, mixed with
charcoal as an explosive.

71 **Commercial Oxygen.**—Although oxygen, in unlimited
amount, is at the disposal of every one, the manufacture of oxygen for
sale has, however, already become a considerable industry. This depends
on the fact that the oxygen in the air is diluted with nitrogen, and,
therefore, in the case of combustion does not produce such a high
temperature as the pure gas. Where, therefore, it is of importance
to obtain very high temperatures, pure oxygen must be employed, and
it must be specially prepared.

The chemical methods employed for this purpose cannot be
discussed here. The preparation from potassium chlorate is too
expensive for the manufacture on a large scale ; other substances are
used which, at certain temperatures, absorb oxygen from the air and,
at other temperatures, give it up again.

Only the principle of one method can be described here. It
depends on the easy preparation of liquid oxygen from the air (see
above). From the mixture of oxygen and nitrogen produced by this
method the nitrogen is removed by partial evaporation. By using
the cold hereby produced for the liquefaction of fresh portions of air,
it is possible to separate the oxygen and nitrogen of the air fairly well
from one another, and this, too, at a price which makes the com-
mercial production appear remunerative.

The oxygen prepared for sale is pumped into steel cylinders (Fig.
       , p.   ) under a pressure of 100 atmospheres, and can be withdrawn
from them with any desired velocity by turning a screw valve. For
the purpose of continuously maintaining definite velocities in spite of
the gradual emptying of the cylinder, there are pressure-reducing valves,
the opening of which enlarges more and more as the pressure in the
cylinder becomes less, and which, in this way, effect a discharge which
is almost independent of the pressure. As a rule, commercial oxygen
still contains 5 to 10 per cent of nitrogen.

72 **Other Properties.** As is to be expected from the great
importance of this element, the measurement of many other properties
has been carried out on oxygen. Their importance is, however, as a
rule, not so great that they should be separately discussed here. One

of them, however, viz. the *solubility in water*, will be given, since it comes under discussion. It is small ; 1 volume of water dissolve 0 , 0·049, and at 20 , 0·031 volumes of oxygen. From atmosph air, in which oxygen is present only to the extent of one fifth, or fifth part will be dissolved. From this it follows that at 0 , 32 of oxygen require 457 lit. of water for solution, when the solutie saturated with pure oxygen If it is saturated with air, 32 oxygen would be contained only in something like 2·3 cubic metre water.

Further, it is deserving of mention that oxygen is *paramagnetic* it is attracted by a magnet, similarly to iron. On account of small density, this property is observable in the case of the gas the case of liquid oxygen, however can be clearly observed.
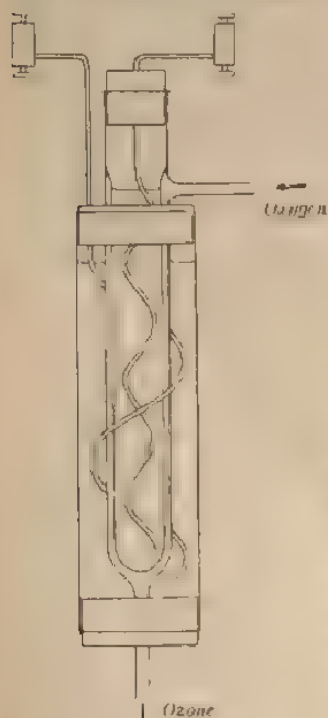
73. **Ozone.**—When oxygen is posed to the influence of electrical ose tions, its volume changes ; the vol contracts and the oxygen, at the s time, assumes new properties. experiment is best carried out in apparatus consisting of two t placed one within the other, and f together. These tubes are coa within and without, with an electr conductor ; each coating is connec with a pole of an induction mach and oxygen is passed in a slow curr through the space between the tubes.[1]

74. **Characteristics.**—That so thing new has been formed evidenced first of all, by the fact the issuing gas has a strong sm which is irritating to the mue membrane and induces coughi Further, a piece of bright *sil* which undergoes no change, either air or in pure oxygen, becomes bl

Oxygen

↓ Ozone

Fig. 19.

when held in the stream of gas. Lastly, a colourless solution potassium iodide (p. 47) becomes coloured dark brown when

[1] An advantageous modification of the apparatus consists in forming both the inner and dilute sulphuric acid which is a fairly good conductor of electricity. (Fig. 19) means of the liquor, the apparatus well being also, is kept cool, a great advantage on the yield, since ozone is destroyed by warming, i.e. it is conve again into ordinary oxygen.

ltered oxygen is conducted through it, whereas ordinary oxygen
has no effect. All these properties are again lost when the altered
oxygen is passed through a heated glass tube.

We here stand face to face with the fact that a simple, or unde-
composable, substance assumes other properties without passing into a
chemical compound by interaction with another substance. For, the
glass of the electrical apparatus, with which the oxygen is in contact
during its alteration, remains entirely unchanged, as also does the
steel tube in which the altered oxygen again passes into ordinary
oxygen.

This oxygen, endowed by means of the electrical treatment with
other properties, is produced also under many other conditions. Even
in very small quantity, it is recognisable by its remarkable smell, on
account of which it has received the name of *ozone*.

Pure Ozone.—The oxygen in our apparatus is converted,
after all, only in small part into ozone, so that the issuing gas is a
mixture of oxygen with a small percentage of ozone. Pure ozone can
be obtained by passing the mixture through a tube cooled by liquid
oxygen the ozone condenses then to a liquid of a corn flower blue
colour, which passes at – 110 into a blue gas. Working with this
is dangerous, since it readily explodes, passing, with development
of heat, into ordinary oxygen.

Relation of Ozone to Oxygen.—This last fact gives us the
key to the understanding of the phenomena. The heat which the ozone
keeps on passing into ordinary oxygen was contained in the ozone,
not, it is true, as heat, but as energy of another form, which is called
own energy. We can, therefore, write the equation

$$\text{oxygen} + \text{energy} = \text{ozone.}^{[1]}$$
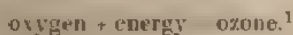
In subjecting oxygen to the influence of electrical oscillations, there
is imparted to it the energy which it requires for its transformation
into ozone.

As is evident, ozone can be formed from oxygen only under such
conditions that the necessary energy can be transferred to the latter.
As a matter of fact, this is the case in all circumstances (to be specified
later which lead to the formation of ozone (*vide* Chap. XV.).

Allotropy. Elements which, by reason of different energy
contents have different properties, are called *allotropic*. Oxygen and ozone
are therefore, *allotropic modifications of the same element*. The fact of
the existence of allotropy follows, on the one hand, from the fact that
the different forms are convertible into one another *without residue*,
and on the other hand, from the fact that equal weights of both forms
are identical products with equal weights of other substances. Thus,
the combination of a combustible substance with oxygen or ozone,

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[1] The equation is not to be thought of as expressing that ordinary oxygen contains
no energy, but only that ozone contains more energy than ordinary oxygen.

exactly the same compounds are obtained, and in these not remains of the difference between the two kinds of oxygen.

Besides the difference in chemical behaviour and in energy-con there also exist between oxygen and ozone differences in their phy properties.   More especially has there to be mentioned that the de of ozone is to that of oxygen as $3 : 2$.   One cc. of ozone weighs, u normal conditions, $0 \cdot 002144$ gm., and 1 gm. of ozone occupies volume $466 \cdot 5$ cc.

78. **Technical Application.**—Since ozone acts more quickly more energetically on oxidisable substances than oxygen, it is prep at the present day, on a large scale, by an electrical method, ar employed in the arts for bleaching, purification of starch, resinific of oils, etc.

79. Preparation from Water.—*Water* is one of the most important and widely distributed compounds of oxygen. Besides oxygen, this substance contains another element which is called *hydrogen*, and which can be obtained from water by the withdrawal of oxygen. This can be done, for example, by means of red-hot iron. We have convinced ourselves (p. 64) that, at a moderately high temperature, iron combines with oxygen. If iron, in the form of thin wire, or turnings, or otherwise finely divided, be heated in a tube to redness
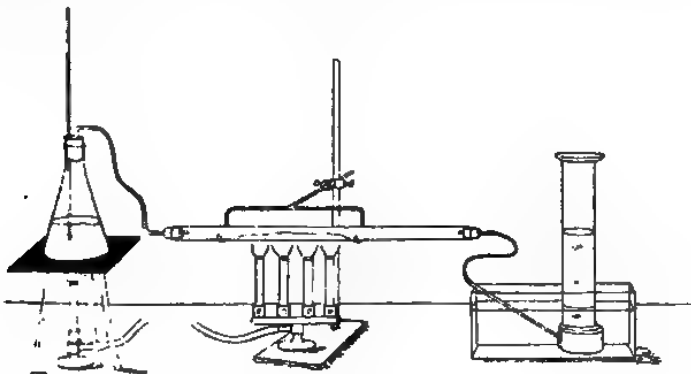
Fig. 20.

and steam be passed over it (Fig. 20), the latter is converted into a gas which can, like oxygen, be collected over water.

80. Identification of Hydrogen.—The gas which is collected resembles oxygen in its outward appearance; like it, it is colourless, odourless,[1] and tasteless, and is not dissolved by water to an appreciable

The gas obtained from steam and ordinary iron exhibits an unpleasant smell, reminiscent of petroleum. This, however, is due to the formation of other substances from the carbon contained in ordinary iron, and does not occur when *pure* iron is used.

extent. It can, however, be readily distinguished from oxygen by
well-known reaction of that gas. A glowing splinter of wood does
inflame, but is extinguished. If, however, a splinter burning w
flame be brought into the gas, it also, it is true, is extinguished
the gas itself takes fire and burns with a pale flame. Hydr
therefore, cannot support the combustion of wood, but is itself
bustible in air.

81. Detection of Oxygen from Water. If the iron be
wards examined, it will be found to be coated with a black grey, fr
mass which has the same properties as the substance produced b
burning of iron in oxygen, and is, in fact, like it, an oxide of
The following process, therefore, occurs :—

<div align="center">water + iron - hydrogen + oxide of iron.</div>

82. Other Methods of Preparation of Hydrogen.—Th
periment just described is of great historical importance since it se
in its day, to prove the compound nature of water (which was form
regarded as an element). It yields, however, little hydrogen, a
inconvenient to carry out.

The experiment becomes much easier when, instead of ir
metal is used which decomposes the water even at a low tempera
This decomposition occurs with the light metals, *e.g. magnesium.*
water be poured over magnesium powder, such as is, at present,
used for the production of a bright, sudden light in photographing
action, certainly, takes place at the ordinary temperature ; on hea
however, till the water boils, a gas is slowly evolved which can
collected in the ordinary way, and can be shown to be hydrogen b
burning with a pale blue flame

The evolution of gas can be greatly accelerated by dissolvin
the water a little magnesium chloride, a salt like compound
magnesium. This does not take any part in the reaction but
dissolves the *oxide* of magnesium which is formed, and thus frees
surface of the metallic particles from the coating of this substa
by which the action of the water is retarded

Lastly, there are light metals which decompose water with ene
even at the ordinary temperature. This is the case, for example,
sodium (p. 52). On bringing a little of this metal in contact
water, an energetic action takes place whereby so much hea
developed that the metal melts. For the purpose of collecting
gas hereby produced, one can proceed as follows.

A little sodium is placed on the water in the trough and pre
under the surface with an inverted spoon made of fine wire-g
(Fig. 21). The evolved gas then ascends through the meshes of
gauze, while the metal is kept back. If the spoon be placed unde
inverted tube, filled with water and standing in the trough, the
can be collected and be shown to be hydrogen

Also, the sodium may be wrapped in blotting-paper (or in wire gauze) and quickly brought under the mouth of the tube by means of tongs. The water then penetrates only after some moments to the sodium, and so acts within the tube, where it acts on the water and evolves gas. In this way also, the gas can be known by its combustibility, as hydrogen

As a rule, the gas so formed burns not with a bright but with a yellow flame. This is due to the presence of drops of liquid, which contain the *sodium* salt which has been

Fig. 21

carried to this the flame owes its yellow colour. If one wishes to avoid this, the gas must be allowed to stand some time till the drops have settled and the gas has become free from fumes

Chemical "Forces." If the methods by which oxygen was obtained are compared with those employed for the preparation of hydrogen, an essential difference is found. Oxide of mercury and potassium chlorate decompose at moderately high temperatures into oxygen and the other constituent, without the participation of any other substance. Hydrogen, however, was obtained, not by the constituent of water being separated as an *element*, but by its passage to another *compound*, and the formation of hydrogen from water takes place all the more easily the more energetically the combination of the oxygen with the substance added takes place, i.e. the more stable the newly formed compound is.

These conditions are also met with in many other cases. If we have a compound of the substances A + B, and bring into contact with it a substance C, which can combine with A to form a very stable compound, then this compound A + C is formed along with the free B

For a long time the following picture was made of these relations— a picture which is still much used, although there are important reasons why it does not prove to be correct. The various substances were imagined as being endowed with forces, in virtue of which they mutually bind one another. If, now, the force between C and A is greater than that between A and B, C must decompose the compound A + B when both come together; A is bound or attracted by C, and B is displaced from its compound with A and set
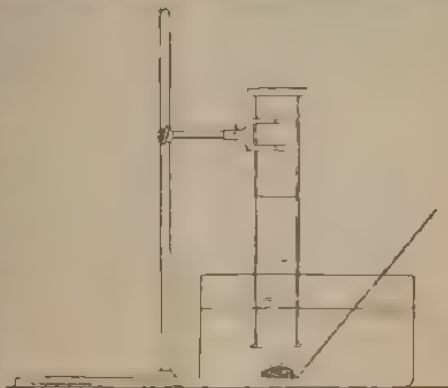
On opening the tap H the air in the apparatus first of all es
the acid flows from C into A, and, when A is filled, comes into co
with the zinc in B.   Evolution of gas begins forthwith, and the h
gen which is generated escapes through the tap H.   If more
developed than can pass through the tap, the acid is forced bac
of B into A and C; it comes out of contact with the zinc, an
evolution of gas is interrupted or diminished.   On the other ha
more gas is withdrawn the acid passes back to the zinc, an
evolution of gas takes place more quickly.

Although this automatic regulation is an advantage, the app
has the disadvantage that the fresh acid from C is mixed with
partially spent acid in A, and its action thus interfered with.
full effect of the acid can, therefore, never be obtained, as can be
with the apparatus first described.

85. **Drying of Gases**. — The hydrogen, which can in this w
obtained in any desired quantity, is not quite pure, since it take
water vapour from the aqueous liquids in the presence of which
produced.   To free it from this, the gas is passed over substi
which retain the water   There are many such desiccating ag
One of the most convenient is *calcium chloride*, a white, very h
scopic salt which is formed as a waste secondary product in
chemical manufactures, and is, therefore, very cheap.   A tube is
with this salt and placed in the path of the hydrogen, the sim
way being to attach the tube directly to the generating apparatu
indicated in Figs. 22 and 24.

Concentrated sulphuric acid is another and much more effe
desiccating agent.   Since this is a liquid it is either placed in a w
bottle (Fig. 25), in which the gas is made to bubble through the li

or spread out over some material which has a l
surface, and is not attacked by the acid, such as br
glass or, better, pumice-stone   It can then be pl
like a solid substance in tubes, and in this case
must only bear in mind that the volume of the
increases through its attracting water and flows d
to the lowest parts of the apparatus.   A collec
chamber for this acid must, therefore, be provi
In Fig. 26 is shown a *drying-tower* which is inter
for large quantities of gas, and which fulfils t
requirements;   it can also be used for calc
chloride.

Besides the aqueous vapour, the hydrogen
quently contains also very fine drops of the li
from which it has been evolved (p. 85).   These pass through w
bottles, but are retained, with certainty, by a plug of cotton wool.

Other impurities which are usually contained in the hydrogen
not occupy us here, since they are mostly of no account for

experiments which are to be performed By these traces of foreign substances, only the fact that pure hydrogen is completely odourless is masked ; impure hydrogen has a slight odour, which it loses, however, by appropriate purification.[1]

86. **Physical Properties of Hydrogen.**—

The most conspicuous property of this element is its small density ; of all known substances it has, as has already been said, the smallest density.

If a flask of about a litre capacity, closed by a stopper and good-fitting glass tap, be weighed, first filled with air and then exhausted, a difference of weight of rather more than 1 gm. is found. If the exhausted flask be filled with hydrogen under atmospheric pressure, the increase of weight amounts to only about 0·1 gm. if anything, rather less. This shows that hydrogen

Fig. 26.

is at least ten times as light as air. By exact experiment the ratio is found to be 1 : 14·4.

On comparing the weights of like volumes of oxygen and hydrogen at 0 and under a pressure of 76 cm., the ratio is found 15·88 . 1 or 16 1·008.

Since 1 cc. of oxygen under normal conditions weighs 0·001429 gm., the weight of 1 cc. of hydrogen, or its absolute density under normal conditions, must be 0·0000900.

87. **Molar Weight.**—This ratio holds, in the first place, for the

two gases under normal conditions. On account, however, of the identity of the laws of pressure and temperature in the case of all gases (pp. 68 and 69), it remains unchanged when the densities of oxygen and hydrogen are compared *at any pressure and temperature*, supposing only that both gases are at the same temperature and pressure. When, therefore, the weight of a gas at any pressure and temperature is compared with that of the same volume of a *normal gas* under the same conditions, a constant ratio-number is obtained which is independent of the pressure and the temperature, and is determined only by the nature of the gas.

For such a normal gas there is taken, not an actual substance, but *an imaginary gas which is 32 times as light as oxygen.* The historical development which has led to the choice of this particular n will be given later (Chap. VII.). For the present, it is suffici state the fact.

The ratio of the weight of a given gas to that of an equal vo of the normal gas under the same conditions is called its *mole*

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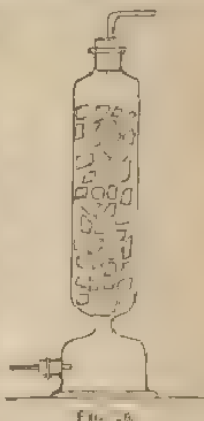
[1] The purification can be effected by means of potassium permanganate contain a wash-bottle through which the gas passes.

weight. Since this name has been derived from certain hypothetical notions regarding the constitution of the gases—notions which are not essential to the actual facts—we shall give preference to the shorter name *molar weight*, although, at present, the other is still the one most used.

Since the normal gas is taken as 32 times lighter than oxygen, its absolute density under normal conditions, *i.e.* at a pressure of 76 cm. and 0°, is equal to 0·00004466 gm. and its extensity to 22,400 cc. Both numbers are of great importance and find manifold application

The *molar weight of a gas* is got, therefore, by dividing its weight G by the weight of an equal volume v of the normal gas under the same pressure p and at the same temperature t. This weight g is found, according to the formula on p. 73, to be

$$g = 0·00004466 \frac{pv}{76(1 + 0·00367t)}$$

The volume is here measured in cc. and the pressure in cm. mercury. If G is the weight of the gas, the molar weight is, according to definition, G/g, or introducing the value of g, the absolute temperature $T = 273 + t$, and collecting all numerical factors,

$$\text{molar weight} = 6234 \frac{TG}{pv}.$$

According to definition the molar weight of oxygen is 32·00. From the data given above for hydrogen, it follows that the molar weight of hydrogen is 2·016.

The molar weight of a gas can also, according to this, be regarded as the weight of that amount of gas which occupies the same volume v, under the same pressure p, and at the same temperature t, as 1 gm. of the normal gas. From the equation $pv = rT$ or $pv/T = r$, we see that the constant r depends only on the pressure, volume, and temperature: it assumes, therefore, the same value for different gases, when these magnitudes are equal. From the definition of molar weight just given, it therefore follows that *the constant r must have the same value for a molar weight of any and every gas*, independent of its nature. The constant referred to the molar weight is called R.

To calculate the value of this, we apply the equation $pv = $ RT to the normal gas at 0° and under atmospheric pressure. In this case, $v = 22,400$ cc, $p = 1,013,130$ in absolute units (p. 68), and $T = 273$. Hence $R = 8·31 \cdot 10^7$ in absolute units.[1] The equation

$$pv = RT = 8·31 \cdot 10^7 T$$

holds, therefore, for a molar weight of any and every gas.

It must, however, be noted that the general gas law, as well as the partial laws (that of Boyle and of Gay-Lussac), is not entirely exact. On the contrary, all gases deviate more or less from it, the deviation being the smaller the more dilute the gases are. We are dealing here, therefore, with a "*limiting law*" (p. 20), to which the actual substances approximate, but which they never entirely fulfil.

Under ordinary conditions of temperature and pressure, these deviations are, in the case of most gases, small, and amount to scarcely a hundredth of the theoretical value. A gas which would completely obey the law $pv = RT$, is called an "ideal gas." The normal gas above defined is assumed to be an ideal gas.

Since, formerly, the densities of gases were, almost exclusively, referred to the density of air as the unit, it is necessary to establish the ratio of our molar weight to these numbers. Now, a litre of air weighs 1.293 gm: it is, therefore, $28\cdot9$ times as heavy as the normal gas. To calculate the molar weight from a density referred to air, the latter must be multiplied by $28\cdot9$; in the reverse case, the number must be divided by $28\cdot9$.

Experiments. The small density of hydrogen can be demonstrated in various ways. A small balloon of collodium, goldbeater's skin, or caoutchouc, is filled with hydrogen and allowed to go free. Since hydrogen is, in round numbers, fourteen times as light as the displaced air, it experiences a corresponding upward force amounting to about 1 gm for every litre, and the balloon, therefore, quickly rises. The same thing can be shown by blowing soap-bubbles with hydrogen and allowing them to ascend.

This property is made use of on the large scale for making air-balloons, which are, essentially, bags of silk rendered air-tight and filled with hydrogen. The total load which such a balloon can carry (inclusive of its own weight) is found, according to what has been stated, to be, in round numbers, 1 kilogm. for each cubic metre. This holds, however, only in the neighbourhood of the earth's surface; the higher one ascends, the less dense does the air become, and the less its buoyancy.

The property of hydrogen can be demonstrated in another way. Two gas-cylinders are filled with the gas over water and supported in the upright position—one with the mouth upwards, the other with the mouth downwards (Fig. 27). If, after a few moments, a flame be brought near both cylinders, the inverted one will be found to be still filled with hydrogen while the other contains only air.

Behaviour of Hydrogen at Higher Pressures.—In its properties as a gas, hydrogen, of all known substances, approximates most nearly to the "ideal" gaseous state. On closer investigation, however, a deviation is found, such that with increasing pressure the volume of hydrogen diminishes *less* than it ought to according to Boyle's law. This deviation increases as the pressure becomes

greater, following a very simple law which can be expressed as follows.

The total volume of hydrogen is made up of one part which strictly follows Boyle's law, and of another part which is independent of the pressure. Denoting the total volume by V, and that part which obeys Boyle's law, and for which, therefore, at constant temperature, the equation $pv = C$ holds good, by v, and denoting by b the other part which is independent of the pressure, we have $V = v + b$. Substituting for v in the equation $pv = C$ its value $V - b$, we obtain $p(V - b) = C$ as the expression for the behaviour of hydrogen at all, and especially at high, pressures.
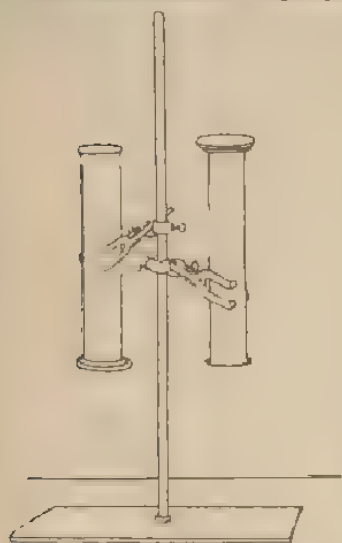
A clear picture of the substance of this law can be got by imagining the hydrogen to consist of small particles of greater density, between which is an empty space. The latter would obey Boyle's law, while the former would represent the incompressible part of hydrogen

In the case of hydrogen at 0 and under atmospheric pressure, the value of b amounts to 0·00062 of the total volume.

The equation $p(V - b) = C$ shows that the diminution in volume is smaller the more the pressure increases, and that when the pressure is very high, V can be only slightly greater than b. In this case, hydrogen behaves almost like a liquid, for a liquid also has the property that its volume diminishes only slightly with great increase of pressure.

* In the case of the other gases, the deviations from the law $pv = RT$ are generally such that the gases are, at first, *more* compressible than according to Boyle's law. At very high pressures, however, they all behave similarly to hydrogen

90. **Liquid Hydrogen**.--By the application of very effective cooling arrangements, the principle of which has been pointed out on p. 78, it has recently become possible to observe hydrogen in the liquid state. It appears as a colourless liquid, the density of which at its boiling point is only 0·07, but which, nevertheless, forms a quite visible surface and exhibits, in all respects, the behaviour of a liquid substance. Hydrogen boils under atmospheric pressure at   252 5 , or only 20 5 above the absolute zero ; by allowing it to boil under reduced pressure, this temperature can only be slightly lowered   At this temperature,

Fig. 27.

...uids and gases [1] (oxygen and air as well) are transformed into ...solids, the vapour pressure of which is exceedingly small. Thus, ... example, if the closed end of a bent tube, filled with air, be placed ... a vessel of liquid hydrogen (Fig. 28), the upper part at once ... free from air and shows a vacuum such as can scarcely be ... with the very best pumps.

... hydrogen was obtained by allowing liquid hydrogen to ... in vacuo. It formed a transparent ice with frothy surface ... melting point lies at about −257°.

Diffusion.—If two cylinders with even ground, broad rims are ... air-tight on one another with the help of a little grease (Fig. 29),

FIG. 28.   FIG. 29.
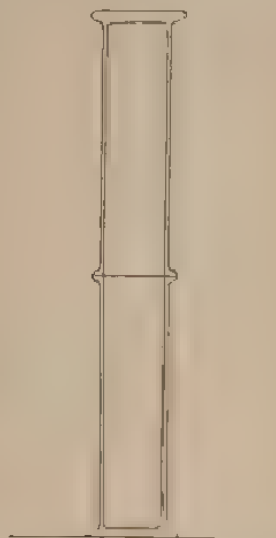
... upper one has been filled with hydrogen, one would expect ... lighter hydrogen would remain above and leave the heavier ... beneath. If, however, on the following day, the two cylinders ... carefully separated from one another and immediately closed ... glass plates which are held in readiness, hydrogen will be found ... For if a flame be brought near, the gas contained in both ... takes fire, and the pale hydrogen flame rushes with a whistling ... along both cylinders.

This mutual spreading of the gases into one another is called

... the exception of helium. Tr.
... the ... admixture of hydrogen here exhibits other phenomena than ... its ... admixture with air, and will soon be explained in detail.

diffusion. It is a quite universal phenomenon; *all gases diffuse* *one another, and the diffusion goes on until each gas is uniformly distri.* *throughout the whole space.*

92. Dalton's Law of Partial Pressures. —Different gases, th fore, which are present in the same space, behave as if each were b alone, for each separately obeys the law that in a given space a g not at rest until it fills the space uniformly. *For gaseous equilibr therefore, not the total pressure, but for each gas only its partial pressure the pressure which it would exert if it alone occupied the space, is of acco*

This is a fact of great importance, since many other phenom exhibited by gases are determined by the partial pressures of th Thus, for example, the partial pressure is the determining factor gaseous equilibrium in chemical processes, which will be conside later.

In order to express these relations for the purpose of calculat one has only to take into account that the total pressure of a gase mixture is the sum of the partial pressures, and that each gas pre is uniformly distributed throughout the space, the total volume be therefore, equal to the volume of each gas. If, therefore, P is

Fig. 40.

total pressure and the total volume, values for the single g being denoted by p_1, p_2 ... and v_1, v_2, v_3 we have the equati $P = p_1 + p_2 + p_3 + $. and v_1, v_2, v_3 ...

The law of par pressures which has j been stated was establish by Dalton, and is cal after him. It is a spec case of a more general la according to which, in given gas mixture (t components of which not chemically interact each single gas behav with respect to all properties, as if it we alone present in the to space under a pressu equal to its partial pre

ure. We shall have many opportunities later of becoming acquaint with individual cases of this general law

93. Velocity of Effusion. A cell of porous clay, such as is us
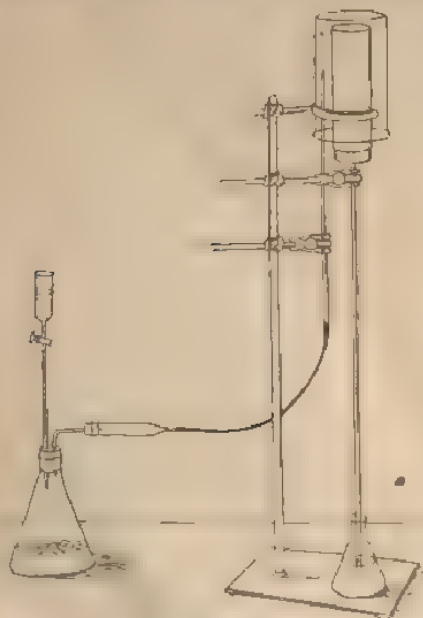
... same batteries, is closed by a cork through which passes a glass ... 1 metre long (Fig. 30). This tube dips into a vessel containing ... water, and a beaker is inverted over the clay cell. If, now, ... current of hydrogen be passed into the beaker, a stream of ... is seen to pass out of the lower end of the tube, which shows ... the pressure in the interior of the cell has suddenly *increased*. ... short time this ceases and equilibrium is established.

If the beaker be now removed, the water ascends just as quickly ... the tube, a sign of *decrease of pressure* in the cell. The water ... a certain height and then sinks again, since the porous cell ... maintain a permanent difference of pressure.

... phenomena are due to the fact that hydrogen passes much ... rapidly than the other gases, *e.g.* air, through small openings ... as the pores of the clay cell. When, therefore, the cell is ... with hydrogen, as in the first part of the experiment, this ... trates rapidly into the interior, since its partial pressure there ... For the same reason, the air passes at the same time out of ... into the hydrogen outside. The movement of the hydrogen ... however, much more quickly, and, therefore, an excess of ... is produced in the interior of the cell, which drives the air ... the tube in bubbles. Equilibrium occurs when the gases on ... of the cell wall have the same composition.

If, now, the external hydrogen is removed, the same processes are ... in the reverse sense; the hydrogen, on account of the differ- ... of the partial pressures, passes outwards, and it does so more ... than the air can penetrate inwards; hence the diminution of ...

... Differences of velocity, similar to those which are here found in ... of diffusion through the pores of the clay, are seen in the case ... diffusion of two gases into one another, without a separating ... Both kinds of movement are, indeed, similar, but we are ... with quite the same phenomenon in the two cases. We ... remark, generally, that hydrogen diffuses more rapidly than ... other gas, and that the velocity of diffusion is, in general, all the ... the greater the density of the gas.

The Law of Effusion of Graham and Bunsen — The ... on the differences of the velocity of effusion of gases in ... we have just been considering, is not suitable for quantitative ... The following, however, is a suitable form.

... apparatus in Fig. 31 is a gas-measuring tube set in a liquid ... two marks m_1 and m_2. At the upper end there is a tap, ... however, does not open free into the air, but into a space closed ... platinum plate pierced with a fine hole. If the tube is filled ... below the mark m_1 with gas and the tap opened, the gas ... through the fine opening, and the time can be noted which ... the liquid passes from the lower to the higher mark

The ordinary light of the sun and of many stars exhibits *black* lines at exactly the same points of the spectrum at which the hydrogen lines appear *bright*. Both kinds of lines are very closely related. At a later stage we shall enter in detail into the relation between them; we would only mention here that these black lines prove the presence of hydrogen with the same certainty as the bright ones. It is, indeed, the same phenomenon appearing under different conditions.

96. Hydrogen burns to Water. —As a test for hydrogen, its combustibility in air has been used. The question as to what thereby becomes of the burning hydrogen can be answered with the knowledge we have already gained. We have seen that iron and sodium, by
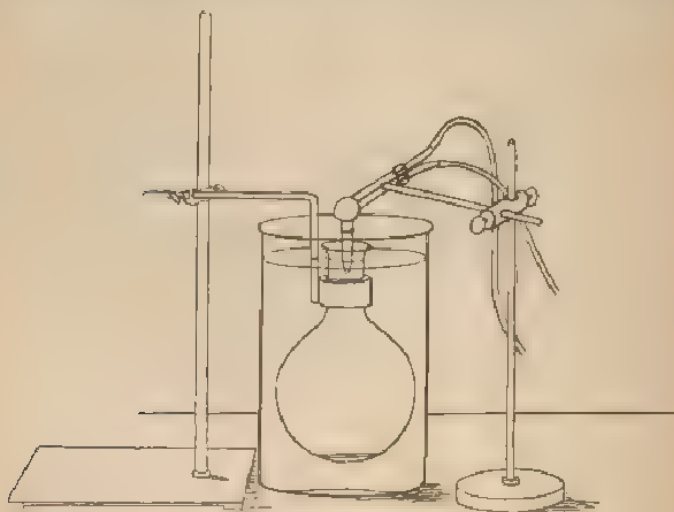
Fig. 34.

acting on water, pass into oxygen compounds, whereby hydrogen is formed. According to this, water is a compound of hydrogen and oxygen, and since combustion consists in a combining with oxygen, we should expect water to be the product of the combustion of hydrogen. As a matter of fact, we can convince ourselves by direct experiment that water is the product of combustion of hydrogen.

If a large, dry beaker be held over the flame of burning hydrogen, a dew is quickly formed which looks exactly like the film of moisture on a cold window pane, and behaves like it. Special arrangements are necessary if it is desired to collect the water in larger quantities.

In Fig. 34 a burner is represented (cf. p. 103) in which, by means of pure oxygen conveyed to it, hydrogen can be burned. Since large amounts of heat are hereby produced, the burner is placed in a wide

glass flask which can be cooled by surrounding it with water.   If this apparatus is put in action, a few cubic centimetres of a colourless liquid soon collect, which, in all its properties, shows itself to be pure water.

97 **Combustion of Hydrogen by means of Oxygen Compounds.** For the formation of water it is not necessary that the oxygen be presented as the free element to the hydrogen; oxygen compounds, or oxides, can also be used for the purpose.   If hydrogen be passed over oxide of mercury placed in a bulb tube (Fig. 35), no action, certainly, takes place at ordinary temperatures ; so soon, however, as the oxide of mercury is *carefully* heated metallic mercury makes its appearance, and *water* is deposited on the colder parts of the tube, first as dew, and then in small drops.
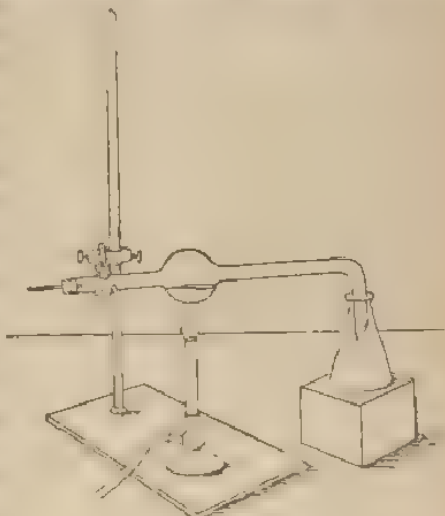
Quite similar phenomena are observed when the oxides of other metals are used in place of oxide of

Fig. 35.

mercury.   By heating *oxide of lead* in a current of hydrogen, metallic lead and water are obtained.   The oxide of lead, under the name of litharge, is obtained in large quantities by heating metallic lead in air, the lead hereby combining with the oxygen contained in the air. When *copper oxide*, obtained by strongly heating copper in air, is heated in hydrogen, red metallic copper and water are produced. Hydrogen may, therefore, be used for the purpose of obtaining the metals from their oxides.   This method finds no application on a large scale, because there are cheaper means of effecting the same result ; for scientific work, however, such methods are, not unfrequently, employed.

98. **Reversed Processes.** —The processes we have just described take place according to a scheme which is similar to that of the displacement of hydrogen from water by iron, only that they represent the reverse process, the displacement of a metal from its oxide by hydrogen (p. 83).

It is therefore of interest to ask whether hydrogen will not also displace the *iron* from iron oxide.   If the previous experiment is repeated, using, however, oxide of iron in place of oxide of mercury quite similar phenomena are, as a matter of fact, observed.   Water

again makes its appearance, and the oxide of iron passes into
This, it is true, does not look like ordinary iron, but has the ap
ance of a black powder. This, however, is due only to the fact
the melting point of iron is much higher than the temperature w
is reached in the bulb ; the iron particles, therefore, cannot unite
coherent mass. If, however, after cooling, the contents of the
are taken out and rubbed with a smooth, hard object, the met
lustre and the grey colour of iron are seen.

The interaction between iron and aqueous vapour can, there
be reversed, and if we write a chemical equation in the form

Iron + water vapour - iron oxide + hydrogen,
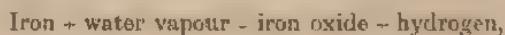
it can be read in *either* direction, the substances on the left b
capable of being converted into those on the right, as wel
conversely. Indeed, more exact investigations have shown that
of these opposed reactions can take place at the same temperature

99. **The Chemical "Forces."** Such a behaviour is contradic
to the notions about "displacement," indicated on p. 85.

In the sense of this theory, the force between iron and oxy
must, according to the experiment described on p. 83, be greater
that between hydrogen and oxygen, because iron decomposes
water Conversely, according to the experiment on p 99, the f
between hydrogen and oxygen is greater than that between iron
oxygen, because hydrogen decomposes the oxide of iron.

Since it is impossible for both propositions to be correct at
same time, it follows that the *theory* which leads to these proposit
must be false.

100 **Mass Action.** As a matter of fact, the investigation of
and of similar cases has shown that not only the nature and, say,
temperature are the determining factors for the occurrence of a chem
process, but also *the ratio of the substances present to the given volume*
the *concentration*, as well. In the present case, the water vapour
on the iron till a certain amount of it has been converted
hydrogen, and a definite ratio between the hydrogen and the w
vapour obtains. Conversely, iron oxide is decomposed by hydro
till a definite ratio is established between the hydrogen remaining
the newly formed water vapour, a ratio which is *the same as*
produced by the reverse method.

A mixture of hydrogen and water vapour corresponding to
ratio acts neither on iron nor on iron oxide. The ratio is, moreov
also dependent on the *temperature.*

The two apparently opposed experiments of p. 83 and p. 99 p
ceed as follows If iron is heated in water vapour a *portion* of
latter is decomposed, and a corresponding amount of iron oxide form
The gas mixture, on being cooled in the pneumatic trough, loses

water vapour it contains, which separates out in the liquid state, and
the hydrogen is collected. This is the experiment of p. 83.

On the other hand, if hydrogen be conducted over hot iron oxide,
a portion of it combines with the oxygen of the latter to form water;
another portion of the hydrogen remains unchanged. On passing the
vapour through the colder part of the bulb-tube the water separates
as a liquid and becomes visible; the remaining hydrogen escapes
unaltered. In this way the notion arises that in both cases entirely
distinct reactions take place.

101. Chemical Equilibrium. — Where two opposite processes
mutually limit one another the state is called one of *chemical equilibrium*.
Whereas formerly the view was held that such a thing occurs only in
exceptional cases, there is now reason to assume that *all* chemical
processes lead to an equilibrium. In many cases of chemical equili-
brium, however, the concentrations of some of the reacting substances,
corresponding to equilibrium, are so small as to escape the ordinary
means of detection. The impression is then produced that the re-
action takes place only in one direction.

A long historical development lies buried in the statement, that at
a given temperature chemical equilibrium is determined by the
condition of the reacting substances. For, although the fact that
the quantity relations of the reacting substances exercise an important
influence on the chemical equilibrium had been already known for
some hundred years, it was a very long time before the correct form
was found for the law which obtains here. From the usual name,
mass action, one might conclude that the mass or amount of the
reacting substances is the determining factor; this, however, is not
the case.

Let us now suppose a state of equilibrium established under given
conditions between the substances just considered—iron, iron oxide,
hydrogen, and aqueous vapour. Push, now, a partition into the
space in which the above substances are contained, so that a part of
the contained gases is shut off from contact with the solid substances; no
change in the equilibrium can be thereby produced. For the gases
are in equilibrium with one another and with the solid substances,
and equilibrium in a uniformly filled space occurs *at every point*, and
cannot, therefore, be dependent on the size of the space filled. By
the separation here imagined, however, the *absolute* amount of the
gases in equilibrium with the solid substances is changed. The abso-
lute amounts cannot, therefore, be determinative for the equilibrium.

By the separation the gases present have been separated *in the
same proportions*, since they were uniformly distributed through the
whole space; otherwise no equilibrium would have taken place. It
is, therefore, the *relative amounts*, or the ratio of the amounts, of the
gases that determine the equilibrium.

The simplest and most appropriate expression for the quantity

... ... non by the non-essential, absolute ... ... volume, or the *concentrations* ... ... This is the expression which we ... ... see from this example of what ... ... magnitudes is, by which we express ... ... ment of the theory of chemical ... ... in the fact that the concentra- ... ... introduced as the determining ... ... attempts had been made to find the

Solid Substances on Chemical Equi- ... as well the special law that *the ... ... in chemical equilibrium*. For ... substances is expressed by their extensities, ... the pressure and the temperature ... small extent that it is of no account

... iron, aqueous vapour, hydrogen, and ... indifferent how much of the two ... oxide, is present, and in what pro-

... somewhat strange, and was formerly, ... One can convince oneself, however, ... by the same course of reasoning as we ... of the gaseous portion; if equilibrium ... cannot be altered by a spatial separation ... which is in equilibrium from the other. ... met with more simple cases of the same ... water and ice, or generally, between a ... form at the temperature of fusion, is ... amount in which the two forms are ... holds for the equilibrium between a ... likewise, also, in the somewhat more ... between a solution and the solid ... is saturated. ... can put forward the general expression, *... portions of the same system the absolute ... and, but only the concentrations within*

... Flame.—The large amount of heat set ... hydrogen causes the temperature of the ... point. In the case of combustion in ... so high, since the heat is distributed ... (p. 61) Much higher temperatures ... in *pure* oxygen. ... take place in the *Darnell Turner* (Fig.

properties in *crystals* which can vary at all with the direction are dependent on this.

In contradistinction to the crystalline substances which possess the peculiarity just mentioned, there are the *amorphous* substances in which that peculiarity is not present. Glass, for example, is an amorphous substance. Two rods, cut in any directions out of a large piece of glass, behave in all respects identically when they have the same shape. On the other hand, two rods of ice, one of which is cut, say, parallel, the other perpendicular to the face of a naturally formed sheet, behave differently; for example, one breaks much more easily than the other.

The crystalline nature is seen most clearly in ice which has been able to assume its shape undisturbed. Thus, the ice on the surface of freezing masses of water first forms in long needles, joined to one

FIG. 49.

other at an angle of 60°, and the ice flowers on window-panes are likewise an expression of the crystalline nature of ice.

The crystals, however, of which *snow* consists can form in the undisturbed manner, for they form floating in the air. As a rule certainly, these crystals are small and indistinct; under certain circumstances, however, they grow so large that they can be seen with the naked eye. They then usually appear as flat stars, developed according to a threefold symmetry. Some snow crystals are shown in Fig. 49.

The property of occurring in crystalline shape is a very wide-spread peculiarity of solid substances, and the formation of crystals may generally be denoted as a property of pure substances. The amorphous state, on the other hand, is confined almost entirely to mixtures. The crystalline form is an important characteristic of solid substances, and we shall repeatedly have an opportunity of discussing such questions later.

117. Supercooling.—The formation of ice in water which has been cooled to 0° does not necessarily occur. On the contrary, with some care, water can be cooled to several degrees below zero without it

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the gas can be redu
ise, but it does not re
of the bell.
amount of water whi
for small operations or

a cylinder inside the vessel of water in such a way as to leave annular space filled with water (Fig. 39). The inner cylinder closed at the top or remain open. In the latter case the space is doubled, but the complete expulsion of the gas is ble. It is the form which is most largely employed, and it principle, more particularly, that the enormous gasometers manufactories are built.

holder without movable parts, which is largely used in nes, is shown in Fig. 40. To use this, it is first filled with and the gas is then introduced either through the tube h or ing the delivery tube of the generator tubulus s. In either case the displaced out through the latter. When has been filled, the tubulus s is a screw cap and the tap h also closed. then poured into the upper vessel. ing the tap w, water flows into the and subjects the gas to a pressure ing to the height of the column Under this pressure the gas when the tap h is opened. When gas is required, the taps w and h
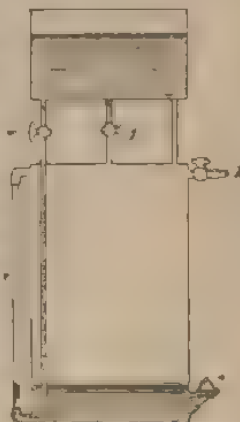
short tube a, which is furnished with can be used for filling larger vessels. placed mouth downwards in the of water over the open end of a. On opening w and a, water down through w, and a corresponding amount of gas escapes

water-level serves to indicate how much gas is present in the when the latter is not made entirely of glass.

Detonating Gas. The Daniell burner is so arranged that gases can only mix immediately before they are burned. If empted to previously mix oxygen and hydrogen, so as to be burn them from a single tube, it is found that the whole mixed gases instantly takes fire and combines with a loud the vessel usually being shattered. This explosion is very with somewhat larger quantities becomes dangerous. One fore, avoid inflaming mixtures of hydrogen and oxygen taking suitable precautions. Such mixtures, called *detonating* always formed when a freshly charged hydrogen apparatus, partially filled with air, is put in use. If the gas which is be collected in small tubes and brought into contact ame, the first samples behave like air and exhibit no special Soon a gas is obtained which takes fire with a whistling

Fig. 40.

noise, the flame rushing into the tube.   These phenomena first be
more marked and then weaker, and, at length, when all the ai
been driven out of the apparatus, the gas burns quietly just as
hydrogen does.

*On account of the danger of an explosion, one must never wait
in the above manner the hydrogen taken from a generator or gas-
which has stood some time, to see if it explodes.*   Should it explode
gas must be allowed to stream for some time out of the gene
until a sample in a small tube is shown, by its combustion, to be
The contents of a gas holder must, without fail, be rejected if
have assumed explosive properties.

The characteristic property of the explosive mixture is seen
clearly by preparing a mixture of two volumes of hydrogen and
of oxygen, and passing it into soap-water, so that a froth of bu
filled with the explosive mixture is formed.   If this froth be s
fire (after the rest of the mixture has been removed) it burns w
report like the shot of a gun.

105. **Further Particulars concerning the Combustion**
Detonating Gas. — While at comparatively high temperatures
combination of hydrogen and oxygen takes place with great viol
the two gases can be left in contact with one another at the ordi
temperature for a very long time without chemical action taking
between them.

This behaviour changes when certain metals are introduced
the gas mixture, and in this respect *platinum* (p. 60) is the
effective.   If a piece of *pure* platinum foil be allowed to project
a tube containing the explosive mixture standing over water,
volume of the gas quickly diminishes, and in certain circumstances
platinum becomes so warm, owing to the heat of combination, th
glows and causes the explosion of the mixture.

Since the platinum foil, being a solid substance, can act only a
surface, its effect increases as the surface is enlarged.   Platinum
be obtained, by means of chemical reactions, in a finely divided, spc
state.   Such *spongy platinum* very quickly becomes incandescent in
explosive mixture and causes an explosion.

To moderate the reaction, the spongy platinum, in the form c
powder, is mixed with clay and formed into balls.   The mass acted
by the heat produced is thereby increased and the temperature
lower ; these balls, therefore, effect a fairly rapid formation of w
from the mixture of oxygen and hydrogen, but not ignition.
apparatus in which this phenomenon can be well shown is represen
in Fig. 41.

Many other metals act in the same way as platinum, most
them, however, only at a somewhat higher temperature.

The platinum, and no less the other metals, undergoes no cha
during this action.   Also, a given small quantity of platinum

convert unlimited amounts of the explosive mixture to water; the action of the platinum, therefore, does not, as in the case of a chemical combination, take place in definite proportions, but is independent of the relation between the amounts of the gas mixture and the platinum.

Reactions of this kind occur very frequently in chemistry. Not only can other gas mixtures be caused to enter into chemical reaction by means of platinum and other metals, but liquid and gaseous substances also can exert such actions in liquids and gases; by means of these, chemical reactions which do not or do not appreciably take place without them proceed rapidly, and the acting substances can cause unlimited amounts of the other substances to react.

106. Catalysis.—For the sake of having a short designation for these important phenomena, we shall call actions of this kind *catalytic*. The substance, through the presence of which the action takes place without itself passing into the products of the reaction, is called the *catalytic substance* or *catalyser*. The process itself is called *catalysis.*

To gain an understanding of these phenomena we recall the consideration put forward on p. 65, according to which innumerable substances, between which chemical reactions could occur, can remain in contact with one another without our being able to detect such actions.

Fig. 40

At that time it was explained that the most appropriate interpretation of these facts is that in all such cases the possible chemical reactions do, as a matter of fact, take place, but to such a small extent or with such slowness that they cannot be detected in a measurable time.

The following shows that this view is quite compatible with the universal experience. By time measurements of the progress of many chemical reactions, the approximate rule has been obtained that the velocity of chemical reactions is, on an average, doubled by a rise of 10 in the temperature. That is to say, if a reaction at a given temperature requires, say, a quarter of an hour to reach a certain point, at a temperature 10 higher it would require only 7½ minutes, and at one 10 lower 30 minutes. If the temperature is lower 100 a 2^{10} - 1024 times longer period is necessary, or in our example about 11 days. On descending farther 50 or, on the whole, only moderate amount of 150, it would be a year before the reaction h proceeded so far as it had done in a quarter of an hour at the high temperature.
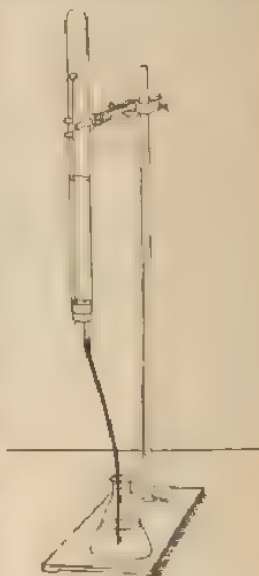
It agrees, therefore, very well with general experience to r
the *possible* chemical reactions in the cases mentioned as a
occurring, and escaping detection only through their very
velocity. So also the height of a hill or the form of a coast ap
to us as something definite and unchangeable, although we know
every hill is unceasingly becoming lower, by the gradual falling
of the rock of which it consists into the valley, and that
coast is changing its shape under the action of the waves.

Substances by whose presence slowly occurring reactions are accel
are designated as positive catalysers. Since we are dealing here only
changes in the velocity of reactions which would take place in
case, these catalytic actions lose to a great extent the quality o
expectedness which at first sight they appear to have.[1]

To obtain a picture of the way in which a catalyser acts, imag
wheel-work in which the axles move with great friction, as a r
say, of the oil having become thick, and which therefore runs
only very slowly. If a little fresh oil be placed on the axle
wheel-work forthwith runs down much more quickly, although
available tension of the spring (which corresponds to the work
able from the chemical reaction) is in no way altered by the oil.
action of a catalyser may be compared with that of the oil in
respect, and also with respect to the fact that the oil is not used
acting

We shall soon have an opportunity of studying other peculiar
of catalytic actions.

[1] Besides the *positive* catalysers or *accelerators*, *negative* catalysers or *retarde*
also known.

CHAPTER VII

WATER

General. The product of the interaction of oxygen and hydrogen, or the compound of these two elements, has shown itself, in all investigations of this point which have been made, to be identical with the water which we find so very widely distributed in nature. In accordance with the law of the identity of the properties in all amounts of a given substance, we may proceed to a scientific investigation of water with that which occurs ready formed in nature, without having first to prepare it for this purpose from its two elements.

Water is one of the most widely distributed substances in nature. Not only are ⅔ths of the earth's surface covered with liquid water, but the atmosphere also contains enormous quantities of water in the gaseous state, and in the polar regions and mountain heights solid water takes an essential share in the structure of the earth's surface. In addition to this the solid portion of the earth's surface is every where permeated with water; water is indispensable for the building up of vegetable and animal structures, and where organic life is, there also is water present.

Preparation of Pure Water. —Naturally occurring water is never quite pure, since it always comes into contact with other bodies and partially dissolves them. The preparation of absolutely pure water is an impossibility, for the very reason that we cannot exclude vessels of some kind, some portions of which can always be dissolved. On the other hand, it is not a matter of very great difficulty to prepare a water which, towards our tests, behaves as pure.

The method most used for obtaining such a water is to convert it temporarily into vapour. The impurities present in natural water are, for the most part, not measurably volatile at the temperature of boiling water, 100°, and therefore remain behind when the water is converted into vapour. Some occasional impurities, however (especially ammonia and carbonic acid), are more volatile than water; they pass over, therefore, almost entirely with the first portions of the vapour.

tains, on an average, only three fourths of this amount.   The a
varies with the state of the weather, and one speaks, therefore, of
or dry air.   Still, air which is called moist scarcely ever conta
much water vapour as it could contain, and air which is calle
may contain as much as half the maximum amount.

The cause of this lies in the great variableness of the vapour
sure with the temperature, as is seen from the following table,
gives the amount of water in grams contained in 1 cc. of air a
saturation point.

Temperature	Water vapour in gr.
0	4·9
5°	6·8
10°	9·4
15°	12·7
20	17·,
25°	22·8

If, at one point, the air has taken up as much water vapo
corresponds to the vapour pressure, and it reaches a place wh
becomes warmer, it becomes unsaturated, i.e. the concentratio
water vapour in it is smaller than corresponds to the equilibrium.
the other hand, if the air falls to a lower temperature, part of
water separates out in the liquid or solid form, as dew, rain, or
and on being heated again to its former temperature the air is
unsaturated.   The differences of temperature, therefore, at the e
surface continually act so that the air contains less water vapour
corresponds to saturation, and for this reason our atmosphere is
completely saturated with water vapour.

The presence of aqueous vapour in the air is so far of import
to the chemist that all objects exposed to the air take up more or
water.   Not only do substances which are soluble in water, suc
salt and sugar, become moist in air containing water, but
insoluble substances, such as glass, stones, metals, textile fa
become covered with a thin film of water, which must, when neces
be taken into account.   The amount of water taken up depends o
nature of the substance, and is, for the rest, proportional to the sur
Bodies with a large surface, powders and cellular structures, suc
are produced in plants, take up a specially large amount of water
responding to their large surface.

" This water does not have the properties of *liquid* water.
only does the object not feel wet, but the *vapour pressure* of this
face held water also is lower than that of liquid water at the
temperature, and it is all the lower the smaller the amount of w
on a given surface.

In many cases it is necessary to remove this water.   For exam
to obtain the exact weight of a body in powder, it must be weig
without its film of water.   The most simple means of freeing the b

...... this consists in *igniting* it, for, as the temperature rises, the vapour pressure of the surface water also increases, and the latter ..... into the relatively dry, hot air. If, however, it is not ... . to raise the temperature of the body, it is dried by being .... in *dry air*. For this purpose glass apparatus, called *desiccators*, .. used, Fig. 53. They contain a substance which combines with .... and withdraws this from the air. Into this dry air there again .... water from the substance to be dried, and this process ... .. until the vapour pressure
.... water on the substance has
.. .. as small as that of the
.... combined with the desiccat-
.. substance.

.... such desiccating sub-
... .. have been previously men-
... .. (p. 88), others will be
.... as occasion serves.

.... the drying process, as
... ., depends on the

Fig. 53

.... .. the water vapour from the body to the drying substance, it
.. .... place all the quicker the more rapid this movement is. If,
.... .., we fill the desiccator with hydrogen instead of with air, the
.. .... dry more quickly, because the diffusion of the aqueous
.... takes place more quickly through the lighter hydrogen than
...... the heavier air. The drying, however, proceeds most quickly
.... .. desiccator is exhausted, because the movement of the aqueous
.... takes place without any hindrance. It would be a mistake
.. .. that the substance could be brought to a *higher degree*
.. .. in an exhausted desiccator than in one containing air, for
.. .... pressure is the same whether air is present or not. The
.... is one of rapidity, and in a given *limited time* a
.... certainly become drier in an exhausted desiccator than
.... air.

.... also take into consideration here, that as the body becomes
.... .. vapour pressure diminishes. Since, now, the passage of the
.... .. the desiccating substance takes place all the more quickly
.. .... the concentration of the water vapour, there lies a retard-
.. .... in the progress of the drying itself. This is a universal
.... When any state of equilibrium strives to establish itself
.... velocity, this velocity diminishes in the same measure
.... of equilibrium is approached, for, in general, the velocity
.... process is proportional to its distance from the position of
....

.... other things it follows from this, that, strictly speaking,
.... of equilibrium will be reached *only after an infinitely long*
.... Since, however, our means of measurement are of limited
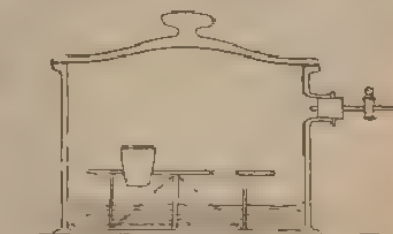
has the form of a tube bent round like a screw, and is made of tin, because this metal is practically not attacked by water. It st in a larger vessel through which water is allowed to flow, in this also from below upwards. The warm water which passes out at top may be suitably used for feeding the still, so as to recover a of the heat. Such an apparatus is represented in Fig. 44.

To demonstrate the effect of distillation, a quantity of wat coloured with ink and distilled from an apparatus, such as is show Figs 42 and 43. The water passes over colourless and tasteless.

109. **Properties—Colour.** At ordinary temperatures w is a transparent, colourless liquid. This absence of colour, howe is only apparent ; in thick layers water exhibits a distinct, fine coloration, which is peculiar to pure water and is not in any way to admixtures. The blue coloration is produced owing to the that water absorbs yellow and red rays, *i.e.* converts them into h when these are withdrawn from white light the complementary colo blue, remains. This blue colour is seen in lakes and seas contain very pure water ; in most cases of naturally occurring water i masked by the presence of coloured admixtures.

110. **Density.** As has already been mentioned, the density of wa has been made equal to unity, the unit of mass, 1 gm., having b ascribed to the unit volume 1 cc. of water. This number, howev holds only for the definite temperature 4 , since the density of wa like that of all other substances, changes with the temperature

In the case of water this change occurs in a manner essential different from that in the case of other substances. On heating wa from 0 upwards the density does not *decrease*, as is usually the ca but it *increases*. At 4 water attains its maximum density, and thi the reason why this temperature has been chosen for the definition unit density. From 4 onwards the density of water, as of all oth substances, decreases with rising temperature, and at 100 amounts about ¹⁄th less than at 0 . The extensity, or the specific volum behaves in the reverse manner ; it has its smallest value at 4 , and all other temperatures its value is greater.

The following table gives a summary of the relation between t temperature and the density and extensity of water :—

	d	e
0°	0·999871	1 000127
4°	1 000000	1 000000
10°	0·999706	1 000265
20°	0·998232	1 001771
30°	0 997705	1 001311
40°	0·99234	1 00773
50°	0·98813	1 01202
60°	0 98331	1 01697
70°	0 97780	1 02260
80°	0 97181	1 02900
90°	0 96550	1 03571
100°	0 95865	1 04315

The same relation can be represented by the geometrical method described on p. 74, the temperatures being taken as abscissae, and the volumes as ordinates.

In this way we obtain Fig. 45, which represents the relation of the volume to the temperature.

The decrease in the density between 0° and 4° is so small that it cannot be represented in the figure. It would mean a lowering of the curve by only 1·5 mm. To represent the scale of tem-

Fig. 45

peratures as well as that of volumes, must be considerably increased. A suitable diagram would be obtained by taking the temperatures ten times, and the volumes a thousand times, as great. Our drawing would, however, thereby become much too large. If, however, we examine Fig. 45 with regard to that portion which interests us just now, we see that there is a large empty space between the curve and the base-line. We can leave this out, and instead of the base-line corresponding to the volume zero, we can choose another near the curve itself. For such a purpose it is well to choose a line corresponding to the volume 1·0000. On this line the temperatures are marked off on a scale ten times larger than before. Perpendicular to it there are marked off, not the volumes themselves, but only their differences from the value 1·0000.

In this way Fig. 46 is obtained. To render the measurement easier the whole field is divided by a rectangular network. In a

Fig. 46
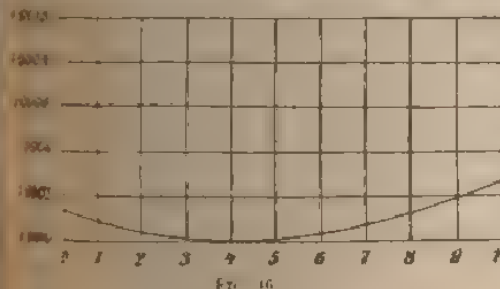
manner which is readily intelligible, the numerals placed at the edges allow of the extensity corresponding to each temperature, and conversely, being read off. The figure is repeated only up to 10.

111 **The Law of Continuity.**—In the table on p. 112 only the densities and volumes corresponding to certain definite temperatures are given. The question

I

now arises as to how the intermediate values, for which there are no data, can be ascertained. For this purpose use is made of a general law, the application of which is so familiar to us that it appears axiomatic, although, like all the other laws of nature, it is a summary of manifold experience.

The law in question is called the law of *continuity*, and is to the following effect :—When two magnitudes change simultaneously with one another, so that for a definite value of the one there is also always a definite value of the other, *the simultaneous changes always remain proportional.* When, therefore, the one magnitude is allowed to increase continuously, the other also increases continuously, and if the one change is made smaller and smaller till it becomes zero, the change of the other magnitude also becomes zero.

It follows from this that when two (not too remote) values A_1 and A_2 of the first magnitude are given, to which there correspond the values B_1 and B_2 of the second, the values of B, corresponding to values intermediate between A_1 and A_2, lie between B_1 and B_2.

If the values A_1 and A_2 are sufficiently close, one may even assume a *proportionality* between the two series of values. If A_x is a value intermediate between A_1 and A_2, and B_x the corresponding value of the other magnitude, we may write the following equation :

$$\frac{A_1 - A_x}{A_1 - A_2} = \frac{B_1 - B_x}{B_1 - B_2},$$

from which we find B_x to be,

$$B_x = B_1 - \frac{B_1 - B_2}{A_1 - A_2}(A_1 - A_x).$$

This formula allows of the calculation of intermediate values which have not been determined, from the measured values on either side of them. It is all the more exact the closer the measured values are to one another. If in any given case it is not exact enough, it can be replaced by a more complicated formula, which also depends on the principle of continuity, which, however, will not be deduced here

The process which we have just described is called *interpolation.* The method will be familiar to the reader from the use of logarithm tables, where the values of the logarithms or numbers not given in the tables are obtained from the adjacent ones by means of such a calculation by proportion.

It lies in the nature of what we have just been considering, that the method can be used only for obtaining *intermediate* values, and may by no means be extended beyond the region of measurement. Such a method —*extrapolation*— is applicable, at most, only in closest proximity to the last point measured, and readily leads to errors if extended

osmotic pressure had been established automatically by the freezing of a little water. Since ice has a volume $\frac{1}{11}$th greater than that of water, the solidification of a small amount in the closed space is sufficient to produce a very considerable pressure.

This peculiarity of ice of melting under pressure has a great influence on the meteorological and geographical properties of solid water. When two pieces of ice are pressed against one another they melt at the surface of pressure; the issuing water which escapes from the pressure forthwith solidifies again, and the two pieces of ice are thus joined together to a whole. This is the cause that loose snow forms coherent masses when it is pressed. As every one knows from making snowballs, this cohering of the snow occurs all the more readily the nearer its temperature is to the melting point, the reason of this clear from what goes before.

The same peculiarity brings it about that the snow on the tops of the mountains gradually passes into *névés*. It also effects the characteristic phenomenon of the *flowing of glaciers*. As is known, the ice-masses move slowly downwards from the heights of the mountains to the valleys, as if they consisted of a semi-fluid mass. This is due to the fact, that at all parts where the ice-mass rests on the ground a liquefaction takes place at those points which are under the greatest pressure, and this causes a sliding. The ice behaves like a carriage with automatic greasing, and so sets itself in motion under its own pressure.

It is easy to convince oneself of this property by pressing lumps of ice together in suitable moulds. Even when the temperature is kept below zero the lumps unite to form clear masses of ice, turned out the moulds like a metal cast.

All solids do not behave like water; in the case of almost all the melting point becomes *higher* and not lower *with increase of pressure*. The difference lies in the fact that water, as contrasted with other bodies, expands on solidification. Substances which have a smaller volume in the solid state than in the liquid exhibit a *rise* in the melting point with pressure.

States of Equilibrium—Law of Reaction.—The relation between the change of volume on solidification and the shifting of the point of solidification with the pressure is not a chance one, but a necessity. It is a case of a universal law that holds for all states of equilibrium. It can be expressed as follows: *If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a change takes place which opposes the constraint, i.e. one by which its effect is diminished.*

Apply this principle, now, to the present case, in which we have a mixture of ice and water at 0 in equilibrium. If we exercise a pressure on the mixture by diminishing its volume the equilibrium is disturbed, and a process must occur by which the pressure is again

partially relieved, i.e. by which a diminution in volume is produced. This consists in ice melting, for liquid water occupies a smaller space than the ice from which it is produced. The melting point of ice must, therefore, sink with pressure.

If, on the other hand, the volume diminishes on solidification, this latter must be brought about by increase of pressure, i.e. the melting point rises with the pressure.

The foundation of the above stated universal law, which has a manifold application in chemistry and physics, lies in the conception of *equilibrium*. By equilibrium we understand a state which tends to re-establish itself when it is disturbed. This tendency finds expression in the occurrence of phenomena which seek to reverse the disturbance, and the general expression of this tendency is the law enunciated above.

* The term equilibrium is, as is known, derived from mechanics. There it is usual to distinguish three kinds of equilibrium stable, unstable, and indifferent. In chemistry the conception of equilibrium as is apparent from the definition just given, is applied only in the form which corresponds to *stable* equilibrium in mechanics.

130. **The Triple Point.** — On applying to water the rule just enounced, that increase of the phases runs parallel with the diminution of the degrees of freedom, we come to the conclusion that it must certainly be possible to have three phases of water side by side, but that such a system has no degrees of freedom left. It can, therefore, exist only at a definite temperature and a definite pressure.

Such a possibility does, as a matter of fact, exist when ice and water are introduced into an empty space. The space then becomes filled with aqueous vapour, and we have ice, water, and vapour side by side.

The pressure is, in this case, equal to the pressure of water at 0°, viz 0·4 cm. mercury ; the temperature is very nearly equal to 0°. It is not exactly equal to this, for 0° has been defined as the melting point of ice under atmospheric pressure ; under the pressure of 0·4 cm. prevailing here, which is almost exactly one atmosphere less, the temperature is therefore + 0·0073° (p. 132). The pressure is, accordingly, a little higher, but the difference does not affect the last decimal in the number stated.

These are the only values of temperature and pressure at which the three phases of water can exist side by side, and any change of one of these values causes the disappearance of the one or other phase. If the pressure is raised, the vapour disappears ; if it is lowered, the water disappears. If the temperature is raised, the ice disappears ; if it is lowered, the water disappears.

Such an invariable point, in which *three* phases of a substance can exist side by side, is also called a *triple point*. Speaking generally every substance will possess a triple point situated in proximity to

the melting point. Since, however, the melting points are scattered over the whole range of the measurable temperatures, so also are the triple points, and many of these are accessible only with difficulty.

131. **Vapour Pressure of Ice.**—As has been experimentally and theoretically proved, water and ice have the same vapour pressure at 0 . It amounts, as already stated, to 0·4 cm mercury.

We may, however, ask how the vapour pressure of water cooled below 0 is related to that of ice at the same temperature. This is explained in Fig. 56. The temperature is measured on the base-line , the vapour pressure curves of the water and of the ice are denoted by w and i. At 0 the two lines cut ; at that point, therefore, the vapour pressure of both forms of the substance water is the same. To the left of this is shown the vapour pressure curve of the supercooled water as an unbroken continuation of that of the warmer water ; it lies above the vapour pressure curve of ice. At the same temperature, therefore, supercooled water has a greater vapour pressure than ice.
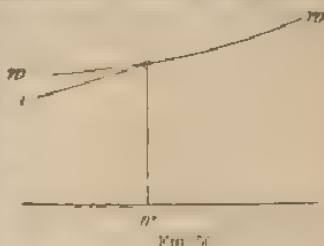
This is the reason why supercooled water cannot exist in contact with ice. Imagine a two-limbed tube, Fig. 57, filled at w with water and at i with ice. At 0 the whole will remain in rest, since the vapour pressure of ice is equal to that of water. At temperatures below zero, however, the pressure above the water is greater than that above the ice. Vapour must, therefore, be constantly given off by the water and be taken up by the ice, and this can cease only when all the water has become converted into ice.

We can now enounce the general principle : *That which is in equilibrium in one way must be in equilibrium in every way ; and that which in one way is not in equilibrium can in no way be in equilibrium.* If, therefore, ice and supercooled water are not in equilibrium as regards their vapours, neither can they be in equilibrium when they are in immediate contact, and in both cases the transformation must occur in the same sense.

The principle of which we have just made use is of the greatest importance, and has a very varied application. It ranks along with the principle of the conservation of energy, and, like it, can be deduced from the impossibility of a *perpetuum mobile*. Whereas the latter principle denies the possibility of creating energy nothing, the former principle denies bility of *setting in motion, for the perf* work, energy which is at rest. In this way, also, a *perpetu* would be possible, as can be readily seen from isolated

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··· ··· ·emistry, since chemical
··· ·· ·stances.   The range of
··· ··· much more limited and
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··· ·· ·requent preliminaries to
··· ·· participating substances

volatile does it take part in the vapour pressure, and then the boiling point may fall through the addition, although the partial pressure of the water vapour in the vapour mixture is always less than the pressure of pure water at the same temperature.

For the rest this influence obeys definite and very remarkable laws, of which we shall presently speak (Chap. VIII.).

The *freezing point of water* is quite similarly affected by dissolved substances, sinking proportionally to the amount of dissolved substance. This law also, like the foregoing one, holds only for dilute solutions.

133. Relations between the Changes of the Vapour Pressure and of the Freezing Point.—The phenomena of the lower ing of the vapour pressure and of the freezing point, through dissolved substances, are interdependent. As was explained on p. 135, water and ice at $0°$ are in equilibrium, because at this temperature both have the same vapour pressure. If, now, the vapour pressure of water is diminished through the solution of a foreign substance, the

FIG. 58.

solution can no longer be in equilibrium with ice at $0°$, but only at a temperature at which both pressures are again equal. If, in Fig. 58, w represent the vapour pressure curve of liquid water and i that of ice, the vapour pressure curve of a solution will, according to what has been said, have the position s. The identity of the vapour pressures of solution and ice occurs at the point where the two curves i and s cut,—in any case, therefore, below $0°$,—and this point will be so much the lower the more the vapour pressure of the solution has been diminished. A constant relation, therefore, which is independent of the nature and amount of the dissolved substance exists between the lowering of the vapour pressure and of the freezing point. Solutions which exhibit the same diminution of the vapour pressure must also exhibit the same lowering of the freezing point. Stated in numbers, the relation is such that a solution whose vapour pressure is $\frac{1}{100}$th less than that of pure water freezes $1·05$ lower than pure water.

The regularities which have been set forth here in the case of aqueous solutions are not restricted to these, *but are, on the contrary, universally valid for liquid solutions of every kind.*

134. Chemical Properties of Water. The reactions which occur by the action of water on other substances are, on the one determined by the fact that it is a derivative of oxygen and hy so that it can give rise to other oxygen and hydrogen compound the other hand, water can combine with substances without the e tion of one of its components. Such compounds are called *hy* from the Greek name for water.
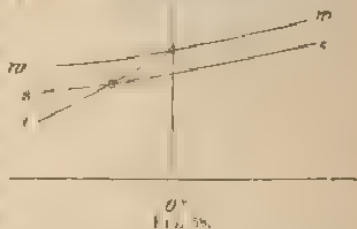
We have already become acquainted with some of the first reactions, namely, those which led to the production of hydrogen, whereby the substances added combined with the oxygen.   Reactions whereby, conversely, the hydrogen is bound and the oxygen set free are also known, and will be discussed later (Chap. IX.).

The compounds produced by the taking up of *both* the elements of water, which are called *hydrates*, are very various in kind.   Many of them can be again very readily resolved into their components ; by a rise of temperature, especially, water is formed from them as vapour. In the case of such hydrates it is usually assumed that they contain the water "as such," in contradistinction to such compounds as do not give off water.   This method of expression, however, has no definite meaning (cf. p. 39), and closer investigation shows that an unbroken transition exists between the two classes, all the hydrates being capable of being arranged in a connected series, according to the ease with which they give off water   The measure of this readiness is the *pressure of the vapour* above these substances at a definite temperature.   We shall enter more fully into these relations at a later point (Chap. XXI.).

Water, likewise, frequently exercises an influence on chemical reactions through its two components, oxygen and hydrogen.   Since, for the reasons just given (p. 136), most chemical reactions are carried out in aqueous solution, we have in all these cases the further possibility of the water also acting chemically.

This consists, essentially, in the fact that in chemical reactions the elements of water can, at the same time, leave or enter a substance If hydrogen be conveyed to a substance containing oxygen, the latter may either take up the hydrogen, or it can also lose oxygen, which is then eliminated with the hydrogen as water.   Likewise, a substance containing hydrogen can, in contact with oxygen, become either richer in oxygen or poorer in hydrogen, the oxygen in the first case being simply taken up, in the second case forming water which is eliminated.

The taking up of oxygen is called *oxidation ;* its withdrawal, *reduction.*   In the sense of what has just been said, however, the result of the oxidation can be a decrease of the hydrogen instead of an increase of the oxygen ; in the same way, a reduction can result in an increase of the hydrogen instead of a loss of oxygen.   In aqueous solution it is frequently not an easy matter to decide which of the two possibilities has occurred.   It is, therefore, generally agreed to regard the taking up of hydrogen also as a reduction in any given case, and the loss of hydrogen as an oxidation.   We shall also continue to use these expressions in the double sense.

135. **The Quantitative Composition of Water.**—The experiments described on pp. 98 ff., which demonstrate the composition of water from oxygen and hydrogen, can by suitable elaboration, be

conductors of the first class. So soon, however, as the current passes from a conductor of the second class to one of the first, in which it flows without the transportation of substance, an accumulation of the transported substances must occur at the junctions of the two conductors, and these substances separate out.

Thus, in water the hydrogen moves with the positive electricity, the oxygen with the negative. At that point, therefore, where the positive electricity passes out, the *cathode*, hydrogen appears; at the point where the positive electricity enters, or where the negative electricity passes out, the *anode*, oxygen appears.

In order to carry out the electrical decomposition, or *electrolysis*, of water, therefore, the latter must be placed between two metallic conductors which effect the passage of the current. The apparatus have different construction, according to the purpose in view. An apparatus, the purpose of which is not to give the most advantageous electrolysis possible, but of a convenient demonstration of the process is represented in Fig. 59.

The water [2] is contained in a U tube, the limbs of which are fairly long and closed at the top by taps. In the lower part of the tube platinum wires are sealed in, and to these are attached two plates of the same metal by means of which the electric current is conducted

Fig. 59

into the liquid. At these plates oxygen on the one side, and hydrogen on the other, are evolved, the gases ascending in the limbs and collect underneath the taps. The displaced liquid passes through a third tube at the foot, and through a rubber tube into a collecting vessel at the side which can be placed in any desired position. After the current has passed some time and a sufficient quantity of gas has been evolved the following facts can be recognised:—

The evolved gases do not occupy the same volume. On the contrary one appears in larger amount, and on making a measurement it is found that its volume is twice as great as that of the other.

[2] In the experiment one does not use pure water, but a dilute solution of sulphuric acid. The reasons for this and also the more exact discussion of the whole process will be given at a later point (Chap. IX.).

_ he volume ratio of
 sity of water vapour
 n gives the volumes
 d in one gm. of water.
 in the vaporous condi-
 drogen which has been
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 ation in a clear manner, by
 and measuring the volume of
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 a current of sufficient potential
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colourless gases, at those points
 the liquid. One of these gases
 kindles a glowing wood-splinter.
 ion, but can be ignited in contact
 ame ; it is therefore hydrogen.
 ion of water by the electric current
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Fig. 59.

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The evolved gases do not occupy the same volume. On the contrary one appears in larger amount, and on making a measurement it is found that its volume is twice as great as that of the other.

[1] For this experiment one does not use pure water, but a dilute solution of *sulphuric acid* or *caustic soda*. The reasons for this and also the more exact discussion of the electrolytic processes will be given at a later point (Chap. IX.)
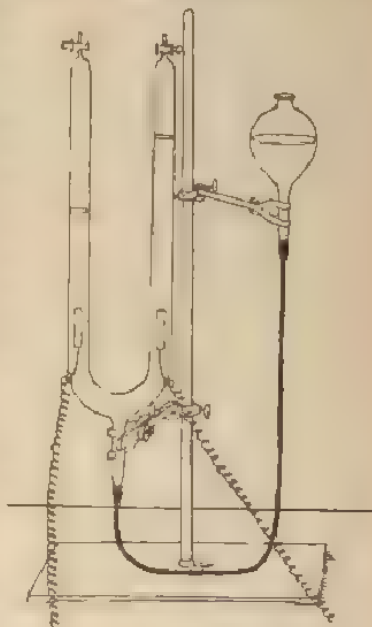
law of the conservation of weight, must also be equal to the *sum of the combining weights of the elements*, or to a rational multiple of this. The values of the combining weights of the compound substances are usually so chosen that they are never smaller than the sum of the combining weights of the elements in order to avoid fractions of the combining weights of the latter.

140. **Combining Weight of Hydrogen.**—In order to choose a value for hydrogen, we can simply assume the combining weight to be proportional to the gaseous density, so that equal volumes of the gases also contain the same number of combining weights. According to the gas-ous densities, then (p. 90), the combining weight of hydrogen must be made equal to 1·008 if oxygen is equal to 16.

A difficulty, however, arises when the product of combination, ... is taken into account. Adopting the stand-point that the .... weights are directly proportional to the gas densities, we deduce for water from the figures on p. 125, the value 9·008. The combining weight of water would, therefore, not be equal to the sum of the combining weights of its elements, but only to half this.

It is, therefore, not possible to make the combining weights simply proportional to the gas densities or to the molar weights (p. 90) ...... falling into contradictions. In the course of the develop-...... hitherto attempts have been made in various ways to remove ...... contradictions. The following is the method now universally

...... *weights are determined so that there is always a whole ...... of combining weights contained in the molar weights.*

If we ..... the molar weight of *oxygen*, as has already been done, ... that of hydrogen to 2·016, the molar weight of ...... must be put equal to 18·016, as can be seen from the ...... 125. If, on the other hand, we put the *combining ...... weight* equal to 16, and that of hydrogen to 1·008, we ...... experiment which has just been stated. The molar ...... and likewise of hydrogen, then contains two com-...... elements, while in the molar weight of aqueous ...... contained two combining weights of hydrogen and ...... of which is equal to the combining weight of ...... this substance, therefore, molar weight and ......

...... shown itself to be sufficient also for all ...... which hydrogen and oxygen are contained. Not ...... substances has exhibited a molar weight in ...... amount than 16 parts of oxygen or 1·008

141. **Combining Weights of the Elements.**—By deter-...... each element combines with one combining

weight, or 16 parts, of oxygen, the combining weight of that element is obtained.

Now, to be sure, it is not necessary to assume that only *one* combining weight of the other elements always combines with one combining weight of oxygen, but, as in the case of water, there may be reasons for regarding other assumptions as better. In fact, there are numerous instances where such is the case. Since these, however, follow only from a more exact knowledge of the chemical relations of the elements, the discussion of them must be postponed, and we shall immediately give the results here.

Farther, the other elements are not all capable of giving compounds with *oxygen*, although the majority of them are. Also, the oxygen compounds of some elements cannot be exactly investigated with regard to their composition, or analysed, so that the question arises how, in these cases, the combining weights are determined.

On this point information is afforded by the definition of combining weight given on p. 143. These numbers are valid not only for the compounds with oxygen, but also for all compounds of the elements with one another. If, then, the fact has been established that an element B combines with oxygen so that for every 16 gm. of oxygen there are present b gm. of the element, and if there be determined the amount c of a third element C which can unite with b gm. of B, then the number c is also the combining weight of the element C.

In general: The weight of an element which can combine with the combining weight of another element, referred to oxygen = 16, is equal to the combining weight of that element.

By means of this principle, it is evident that the combining weight of one and the same element can be determined in very different ways, and through the medium of entirely different elements. This has, in fact, been done, and the combining weights, determined by such different methods, have always proved to be identical within the limit of the experimental error. In these investigations we have an exceedingly important confirmation of the law of combining weights.

The following table gives a list of the combining weights of the elements so far as known with some degree of accuracy; the values are given such that there may be an error in the last place of less than half a unit.

TABLE OF THE COMBINING WEIGHTS OF THE ELEMENTS

1	Aluminium	Al = 27.1	9.	Bromine	Br = 79.96
2.	Antimony	Sb = 120.2	10.	Caesium	Cd = 112.4
3	Argon	A = 39.9	11	Caesium	Cs = 133
4	Arsenic	As = 75.0	12.	Calcium	Ca = 40.1
5	Barium	Ba = 137.4	13.	Carbon	C = 12.00
6	Beryllium	Be = 9.1	14	Cerium	Ce = 140
7	Bismuth	Bi = 208.5	15	Chlorine	Cl = 35.45
8.	Boron	B = 11.0	16	Chromium	Cr = 52.1

TABLE OF THE COMBINING WEIGHTS OF THE ELEMENTS—*coi*

17.	Cobalt	Co	59.0	48.	Platinum	Pt
18.	Copper	Cu -	63.6	49.	Potassium	K -
19.	Erbium	Er -	166	50.	Praseodymium	Pr
20.	Fluorine	F -	19	51.	Rhodium	Rh -
21.	Gadolinium	Gd	126	52.	Rubidium	Rb
22.	Gallium	Ga	70	53.	Ruthenium	Ru
23.	Germanium	Ge	72.5	54.	Samarium	Sa =
24.	Gold	Au	197.2	55.	Scandium	Sc -
25.	Helium	He -	4	56.	Selenium	S -
26.	Hydrogen	H -	1.008	57.	Silver	Ag -
27.	Indium	In =	114	58.	Silicon	Si =
28.	Iodine	I	126.85	59.	Sodium	Na =
29.	Iridium	Ir -	193.0	60.	Strontium	Sr =
30.	Iron	Fe	55.9	61.	Sulphur	S -
31.	Krypton	Kr	81.8	62.	Tantalum	Ta -
32.	Lanthanum	La	138.9	63.	Tellurium	Te =
33.	Lead	Pb =	206.9	64.	Terbium	Tb =
34.	Lithium	Li =	7.03	65.	Thallium	Tl =
35.	Magnesium	Mg	24.36	66.	Thorium	Th -
36.	Manganese	Mn =	55.0	67.	Thulium	Tu =
37.	Mercury	Hg -	200.0	68.	Tin	Sn -
38.	Molybdenum	Mo	96.0	69.	Titanium	Ti =
39.	Neodymium	Nd	143.6	70.	Tungsten	W =
40.	Neon	Ne -	20	71.	Uranium	U =
41.	Nickel	Ni	58.7	72.	Vanadium	Vd =
42.	Niobium	Nb	94	73.	Xenon	X =
43.	Nitrogen	N	14.04	74.	Ytterbium	Yb =
44.	Osmium	Os	191	75.	Yttrium	Y =
45.	Oxygen	O =	16.00	76.	Zinc	Zn =
46.	Palladium	Pd	106.5	77.	Zirconium	Zr =
47.	Phosphorus	P	31.0			

A glance at the table shows that the combining weigh
within very wide limits, in round numbers, from 1 to 240.
these they are distributed pretty uniformly over the whole
numbers.

It is also remarkable that the combining weight of hydr
as can be seen from the table, so near unity, without being exact
to it. This has the following historical reason. The combining
were at first so determined that hydrogen was put equal t
Since, however, only very few elements are capable of forming b
compounds, the indirect method just described had to be app
determining their combining weights. This was carried out b
taining the combining weight of oxygen with reference to h
= 1, and then referring the other elements, by means of their
compounds, to the number for oxygen thus determined, wh
been found equal to 16.00. For such elements, in the case o
oxygen compounds could not be investigated, measuremer
carried out with the help of elements whose combining weig
been determined with reference to oxygen and not to hy
Oxygen was, therefore, the practical basis of *all* the combining

d hydrogen was only chosen formally as such because its combining weight was the smallest of all.

In recent times, now, the discovery was made that the ratio 1 : 16 for hydrogen : oxygen, had been rather inaccurately determined, and that it is really 1.000 : 15.88, or 1.008 : 16.00. The choice had, therefore, to be made as to which of these two relations should be retained, and the decision was given in favour of the second. The essential reason for this was that the number 16 for oxygen had, from always formed the real basis of all determinations and calculations with the combining weights. If, therefore, the number 16 were changed to 15.88, all numbers referred to it must also be changed. By retaining, however, the number 16 for oxygen, and changing only that for hydrogen from 1 to 1.008, no such recalculation of the other numbers was required, since only the value for hydrogen was affected. For the future, then, the number 16 has been adopted as the basis of the combining weights of the other elements.

142 The Accuracy of the Law of Combining Weights.— Since the gas law is only a limiting law (p. 91), and since we have based the law of combining weights on it, the question must arise as to what degree of accuracy this law possesses, and whether it also is to be regarded as a limiting law.

Experience has shown that *the law of the combining weights is as exact as is that of the conservation of weight*, i.e. the limit of its accuracy has, as yet, not been found.

This is connected with the circumstance that the law of combining weights remains valid whether we are dealing with gases or with substances in any other physical state. The *deduction* of the law from the properties of gases was made for the sake of clearness; its *foundation* in fact, however, is the result of quantitative chemical analysis.

143 Chemical Symbols and Formulæ.— Since all compound substances can be represented as combinations of the elements, their composition can be stated by designating the elements from which they are produced. This designation takes a very simple form when, instead of the names of the elements themselves, abbreviated, readily legible symbols are employed.

Such a method has been in use almost as long as chemical writings exist; for even in the oldest alchemistic works the most important of the substances occurring are represented by individual symbols. Traces of such a symbolic language also exists throughout the whole development of scientific chemistry. These very manifold attempts, however, received a permanent form only after the law of combining weights was discovered, and after Berzelius had made an exceedingly simple and suitable proposal for fixing the symbols.

Whereas, namely, all former symbols had been more or less arbitrarily chosen and offered no hold to the memory, Berzelius chose them from the names of the elements themselves, introducing

the initial letter of these as symbol for the element. In order to put differences in language out of account, he used the Latin or Greek names as the basis of the abbreviations. In those frequent cases where several elements commence with the same letter, the aid of an additional characteristic letter is taken.

In this way the symbols given in the table on pp. 145 and 146 were obtained.

While, in former times, such symbols had only a qualitative signification, the law of combining weights makes it possible to attach to them also a quantitative meaning. This consists in also understanding by the symbol of each element a *combining weight* of that element. The symbol O for oxygen, therefore, not only signifies that element, but also 16 parts of it by weight.

Since the combinations between the elements take place only in the proportions of the combining weights and of whole multiples of these, it is only necessary, in order to state the qualitative and quantitative composition of a *compound*, to write down the symbols of the elements present and the factors by which the combining weights of each have to be multiplied. For the sake of convenience it has become customary to write the factors in the position of suffixes to the symbol of the element. The composition of water of two combining weights of hydrogen and one of oxygen is, therefore, written in the form H_2O, the factor 1 being, as is usual, omitted.

This formula expresses the fact that water is produced from 2×1.008 parts of hydrogen and 1×16.00 parts of oxygen by weight, and that it contains these and no other elements.

In the case of substances whose gaseous density and molar weight can be determined, it is further usual to write the formulæ so that they express a molar weight of the substance designated. Since the combining weights were chosen on the principle that a *whole* number of combining weights is contained in a molar weight, this can always be done without having to use fractions of a combining weight. Such formulæ, therefore, allow also of deducing the gaseous density, to which, of course, the molar weight is equal.

114. Chemical Equations. -By reason of the laws of the conservation of weight and the conservation of kind (p. 60), chemical processes can be written in the form of equations in which the substances are represented by their symbols. As a result of the two laws named, we have, first, that the *weights* on both sides of a chemical equation must agree; and, second, that on each side of the equation *the same elements with the same number of combining weights must occur.* The way, however, in which the elements are combined with one another can be different.

For example, the formation of water from oxygen gas and hydrogen gas is expressed by the following equation:

$$O + 2H = H_2O.$$
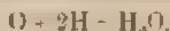
is usual to write the equations in such a manner that the
substances stand on the left hand, and those formed in the
on the right. Since at a very high temperature water
goes into its elements, this process would be written in the
cooler —

$$H_2O \quad O + 2H.$$

can be seen, when more than one combining weight of the
does under consideration takes part in the reaction, the corre-
g factors are written *before* the formula, whereas the factors of
ments which are present in more than one combining weight
(such as hydrogen in water) are written as a suffix

is very frequently the case, it is desired to express, at
time, by means of the formula, the molar weight of the
designated, the equation has, generally, to be written
A molar weight of hydrogen and of oxygen each con-
combining weights of the elements; we must, accordingly,

$$2H_2 + O_2 - 2H_2O.$$
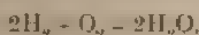
such an equation we can, at the same time, from the
of a molar weight, tell the *volume* ratios of the reacting
The present example shows directly that one volume of
and two volumes of hydrogen yield two volumes of water

formula which signify molar weights are not as yet dis-
from those intended only to denote combining weights.
be called an imperfection. In this book molar weights,
are known, will generally be written.

The Atomic Hypothesis —For the representation of the
comprehensive laws to which the weight and volume ratios
cal compounds are subject, a hypothetical conception has been
the time these laws were first discovered, which affords a
venient picture of the actual relations, and possesses, there
great value for the purposes of instruction and investigation.
reason the above hypothesis has been made the basis of
and modes of representation throughout the whole of
so that the results of chemical investigation are almost
communicated in that language. For this reason alone
edge of the hypothesis is necessary.

general, an hypothesis is an *aid to representation*. Of the
of the outer world, some are so familiar to us from
experience, that we know the relations which exist
them with great certainty. If now we find a new and un-
class of phenomena, we unconsciously seek for similar ones

among those that are known. If we succeed in discovering such similarity we gain two advantages. In the first place, the fixing the new facts in the memory is very greatly facilitated by the use the similarity, and in the second place, the similarity affords the means of making probable *presumptions* concerning the behaviour the new phenomena under conditions under which they have not been investigated.

* As compared with the less known, such a group of similar well known phenomena form the basis of the hypothesis. Since all phenomena those of *mechanics* are usually the most familiar to by far the most hypotheses are mechanical analogies of non-mechanical phenomena.

* The same character is possessed also by the present hypothe The peculiarities of the weight relations of chemical processes "explained" by a definite assumption concerning the mechanical nature of the substances.

This assumption consists in regarding all substances as compos of very small particles or *atoms*. The atoms of each elementary stance are alike among themselves, and single, and are different fr the atoms of every other element. The atoms of a chemical compo are alike among themselves, but are composed of the atoms of elements by the interaction of which they are produced.

From these assumptions the laws of chemical combination foll directly. The assumed identity of the atoms or the atomic grow which form a definite substance gives a picture of the theorem of definiteness of the properties of every substance. The assumption the difference of the nature of the atoms of the different elemen explains the inconvertibility of the elements into one another, a the assumption that the atoms of the elements remain intact in compounds, and are only differently grouped together to form, in e case, an atom of the compound, makes the law of the connectio between the derivatives of each element clear.

On the same foundation also, the *quantitative* laws of combination are made intelligible. Since all the atoms of a definite element assumed to be identical among themselves, we must also assum identity for the weight of each atom When, therefore, two or mo different atoms combine in a definite manner to form a compound, th proportions by weight in which the compound is formed are also fixe by the number and kind of the elementary atoms. Since, finally, compounds are regarded as congeries of the corresponding elementar atoms, the proportions by weight of these must be represented unive sally by the numbers which are obtained by multiplying the weight each kind of atom by the number of them. In this picture, therefore the combining weight of an element assumes the signification of th weight of an atom, and the designation *atomic weight* in place of com bining weight has a universal currency.

Within the limits here given, the atomic hypothesis has proved an exceedingly useful aid to instruction and investigation, since greatly facilitates the interpretation and the use of the general laws. It must not, however, be led astray by this agreement between picture and reality, and confound the two. So far as we have treated them, the chemical processes occurred in such a way as if the substances were composed of atoms in the sense explained. At best it follows from this the *possibility* that they are in reality so; not, however, the *certainty*. For it is impossible to prove that the laws of chemical combination cannot be deduced with the same completeness by means of quite a different assumption.

One does not require, therefore, to give up the advantage of the atomic hypothesis if one bears in mind that it is an illustration of the reactions in the form of a suitable and easily manipulated picture, but which may, on no account, be substituted for the actual reactions. One must always be prepared for the fact that sooner or later the reality will be different from that which the picture leads us to expect.

Especially, when any other well-founded speculation leads to a variance with the atomic hypothesis, one must not, on that account, regard the speculation as wrong. The blame can quite well attach to the hypothesis.

The atomic hypothesis, in the sense developed here, was put forward by J. Dalton in the year 1803; the testing of its most important consequence, the law of combining weights, was performed by Berzelius (p. 113). On account of its entire agreement with experiment the atomic hypothesis attained to a position of great consideration and universal application, so that, even at the present day, it rules almost exclusively in chemistry.

In this book also we shall not deviate essentially from the general usage. Still, it would certainly be to the interest of the science if greater care were exercised in this connection, and for that reason we have been laid stress on using the forms of expression of the atomic hypothesis as sparingly as ever the present usage of language will permit.

The Molecular Hypothesis.—Just as the laws of weight of chemical processes, so also the laws of *volume* in the interaction of gaseous substances have given rise to mechanical hypotheses, which have played a similar though not so important a part in the development of chemistry as the atomic hypothesis.

Since gases combine in equal or in multiple volumes, the most obvious assumption is that the same number of atoms is contained in equal volumes of the different elementary gases. In fact, this assumption was at first made.

With this assumption, however, the fact that *two* volumes of hydrogen and one volume of oxygen yield two volumes of aqueous

vapour cannot be brought into agreement. For, let the number atoms in the unit of volume be X, and let us make the appropri assumption that the same law holds also for the aqueous vap 2N atoms of water must be produced from N atoms of oxygen and atoms of hydrogen, *i.e.* in each atom of water *half* an atom of oxyg must be contained.

This is not the only difficulty of this kind ; on the contra similar ones are encountered in nearly every case of combinati between gaseous substances

To avoid this contradiction, therefore, it was necessary to di tinguish between the *atoms* and the *smallest particles of the gases*, we assume that the latter, which are called *molecules*, are compo of several atoms, the volume ratios of the gases can be satisfactor represented.

The consideration of all known cases has shown that a very sim assumption suffices here. The contradiction can be avoided if, in case of the elementary gases, *e.g.* oxygen and hydrogen, the molecu are regarded as being formed each of *two* atoms. In the case of oth elements other assumptions are in part necessary, and these will discussed when we come to them.

According to this assumption there are contained in *equal volu* of the different gases, not an equal number of atoms, but an eq *number of molecules*. If, as mentioned, the molecules of oxygen a hydrogen each consist of two atoms, and if N is the number of mol cules (not of atoms) in the unit of volume, we have the followi calculation :—

One volume of oxygen contains N molecules, and therefore 2 atoms. With two volumes of hydrogen (– 4N atoms) it forms tw volumes of aqueous vapour, in which, therefore, 2N molecules water must be contained If one assumes that each water molecu consists of one atom of oxygen and two atoms of hydrogen, exactl 2N molecules of water vapour can be formed from the atoms presen and the actual relations receive a correct representation

The molecular hypothesis stands to the conception of the mol weight (pp. 90 and 144), previously introduced on the basis of the la of Gay Lussac, in the same relation as the atomic hypothesis stands the conception of the combining weight, and the molar weight appear in the light of the hypothesis, as the relative weight of a molecule, o the *molecular weight*. For, if an equal number of molecules is assume in equal volumes of the different gases, the weights of the differe molecules must be to one another as the weights of equal gas volume *i.e.* as the gaseous densities or the molar weights.

The requirement that the molar weights shall be expressible i *integral* values of the combining weights assumes the clearly u telligible form, that no fractions of atoms are to be assumed in th molecules.

The name molecular weight is in general use for the previously developed conception of the molar weight. It may also be employed independently of the hypothesis on which it is based, if one bears in mind that it expresses an actual relation, viz. the gaseous density.

The hypothesis just developed was put forward by Avogadro and Ampère almost simultaneously in the years 1811 and 1812. The assumption that in equal volumes of gases equal numbers of molecules are contained is sometimes called the *law* of Avogadro. This is misleading, since a hypothesis can never be a law. It may be called the *rule* of Avogadro. The *law* on which these considerations are based is that of the rational volume ratios in the reactions between gases, discovered by Gay-Lussac.

147 **The Action of Sodium on Water.** — Of the changes which take place by the interaction between water and sodium (p. 84), we have, as yet, considered only the evolution of hydrogen from the water. We shall now pass to the investigation of the other products.

In the first place, the water which had been used for the reaction is in its outward appearance, unchanged; the product which has been formed from the sodium must therefore be *soluble* and yield a *colourless* solution. That something new is present, is shown, however, by the taste, which is unpleasantly soap-like, and by its power of exhibiting reactions not shown by water. One of the most conspicuous of these reactions is the alteration of certain colouring substances. A piece of paper coloured purple with litmus (a colouring substance extracted from lichens) immediately becomes blue when moistened with the liquid formed. A piece of colourless paper containing the artificial dye-stuff *phthalein*, which is used by electricians as "pole reagent paper" for determining the direction of the electrical current in a conductor, becomes coloured purple-red, and paper coloured with the yellow vegetable dye *turmeric*, becomes red-brown.

What takes place in the case of these changes cannot be explained as yet; they serve, in the first place, as an identification sign for the substance produced.

To obtain this substance in the pure condition, the water in which it is dissolved must be removed. This is done by heating the solution until it boils; the water then passes into the form of vapour and escapes, while the dissolved substance, which is not volatile, remains behind.

This method which is generally used for obtaining the substances present in solutions when they are not or are only slightly volatile, is called *evaporation*. The apparatus used for the purpose vary according to the scale on which the operation is carried out: they all agree, however, in being of such a shape that the surface of the evaporating liquid is kept as large as possible. For the velocity of evaporation, or the amount of liquid evaporating in unit time, increases, *cæteris paribus*, proportionally with the evaporating surface.

148. Caustic Soda.—On evaporating the solution produced
the action of sodium on water, a white substance is obtained which
solid at ordinary temperatures, but which readily fuses and redissol
in a small quantity of water with development of heat. It is the sa
substance as served in the combustion experiment described on p.
for retaining the gaseous and vaporous products of combustion I
little of the substance be dissolved in water the liquid exhibits all t
colour reactions of the solution produced by the action of sodium
water.

That this substance also contains oxygen as well as sodium follo
from the fact that it was formed, with evolution of hydrogen, fro
water and sodium ; in it there must be present the oxygen which w
previously in combination with the hydrogen evolved   The produ
however, need not consist of sodium and oxygen *only*, it may a
contain hydrogen from the water.

That it does, in reality, still contain hydrogen is shown by th
following experiment.   If a little of the substance is mixed with fine
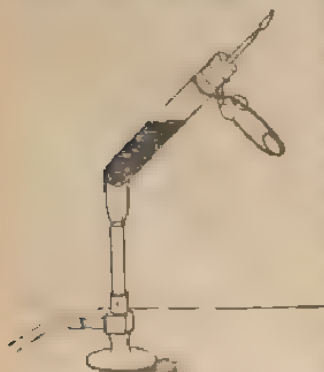
powdered iron, and the mixture heat
in a small tube of resistant glass, clos
by a cork through which a drawn-o
glass tube passes (Fig. 60), there soo
escapes from the opening a gas which c
be set on fire, and can be immediate
identified as hydrogen by the film
moisture formed on a cold glass he
over it.[1]   Since the iron, being
"element," contains no hydrogen th
must come from our substance.

The result of more exact analy
shows that the product consists
sodium, hydrogen, and oxygen in th
proportions 23·05 : 1·01 : 16·00
weight. It contains, therefore, an equ

number of combining weights of hydrogen and oxygen. The co
bining weight of sodium has been found equal to 23·05 ; since th
chemical symbol for sodium is Na, the formula NaOH is obtained f
the compound. In chemical language it is called *sodium hydroxide,*
caustic soda.

The name sodium hydroxide is intended to indicate that, besid
oxygen, hydrogen is also contained in the compound.

Compounds which are constituted in the same way as sodiu
hydroxide, *i.e.* which, along with the metal, contain an equal numbe
of combining weights of oxygen and hydrogen, occur in large number
for almost every metal can form such compounds. In consequence

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[1] The flame of the hydrogen is generally coloured yellow, and this from the sa
cause is given on p. 85.

...er containing these elements in common they possess certain con
...mon properties, so that it has been found convenient to give
...a special family name, and also to give a special designation to
...group OH. The metallic compounds are called *bases*, and the
...OH, *hydroxyl*. *Bases are, therefore, compounds of metals with*
...

...all the metals combine with hydroxyl in such a way that to
...combining weight of the metal also *one* hydroxyl is present. On
...contrary, other reasons have often led to assuming combining
...for the metals such that two, three, and even four hydroxyl
...are united with one combining weight of the metal. The
...corresponding hydroxides or bases then have the formulæ $M(OH)_2$,
...$M(OH)_4$, where M is the symbol of the metal. These metals,
...the bases produced from them, are accordingly called *di-, tri-,*
...*valent.*

...bases, in so far as they are soluble in water, all behave in the
...way as caustic soda with respect to the colouring substances.
...reactions, then, belong, not to the different metals from which
...bases have been produced, but to the common component,
...

Deliquescent Substances. —On evaporating solutions of
...soda it is found that the last portions of water are difficult to
...since the vapour pressure of the concentrated solutions is very
...smaller than that of pure water.

...versely, caustic soda, freed from water, has the property of
...moist in air by condensing on itself the aqueous vapour
...in the latter (p. 125), and it ultimately takes up so much
...that it liquefies to a solution. Caustic soda, therefore, is called
...substance.

...property of deliquescing is not one belonging exclusively to
...soda, but also belongs to many easily soluble salts. The con
...for it is that a solution is produced which has a smaller vapour
...than the mean vapour pressure of the water in the air. Such
...stance continues to withdraw water from the moist air until the
...pressure of the water vapour becomes equal to that of the
...produced. If the air is renewed, as in the case of substances
...open vessels, the process comes to an end only when a solu-
...been produced, the vapour pressure of which is equal to the
...pressure of the water in the air.

...on an average, the air is saturated with aqueous vapour to
...content of 60 to 70 per cent, all substances will deliquesce which
...solutions the vapour pressure of which is less than 0·6 of
...of water at the same temperature.

CHAPTER VIII

150 **Hydrogen Peroxide**.—By means of reactions, the details of which cannot be understood till later (Chap. XXV.), it is possible to prepare a second compound of hydrogen and oxygen which has a different composition and essentially different properties from water. This compound is called *hydrogen peroxide*, a name which expresses that it contains more oxygen than water, which would have to be called hydrogen oxide.

The composition of hydrogen peroxide is given by the formula H_2O_2. This states that for the same amount of hydrogen double as much oxygen is contained in the new compound as in water. In numbers the formula shows that the compound is composed of 2×1.00 parts of hydrogen and 2×16.00 parts of oxygen, by weight; its molar or molecular weight, therefore, amounts to 34.016. If the weights of oxygen and hydrogen present are divided by this number, and multiplied by 100, the percentage composition of hydrogen peroxide is obtained. The result is 94.1 per cent oxygen and 5.9 per cent hydrogen.

Hydrogen peroxide is a thickish liquid with a density 1.5, and is colourless. It is not easily prepared quite pure, and when it is obtained it very readily decomposes spontaneously, so that its existence is always only a passing one. The decomposition takes place according to the equation

$$2H_2O_2 = 2H_2O + O_2,$$
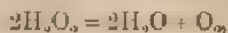
i.e. the substance decomposes into water and oxygen gas.

Nevertheless, by cooling very concentrated solutions, hydrogen peroxide has recently been obtained in the form of clear crystals melting at -2.

On account of its great readiness to decompose, hydrogen peroxide is usually prepared and used in the form of a *dilute solution*, in which it is much more stable. Since it dissolves in all proportions in water, solutions of any desired strength can be prepared, and the strength is

156

usually stated by the number of volumes of oxygen which can be evolved from one volume of the solution on decomposition   Since 2 · 34 gm. of peroxide evolve 32 gm. of oxygen, which under ordinary conditions occupy a volume of 22 4 lit. (p. 90), it follows that every gram of peroxide evolves 353 cc. of oxygen. A one per cent solution, containing, therefore, 1 gm. in 100 cc., accordingly evolves 3·53 times its volume of oxygen, and the solution ordinarily used of strength 10 volumes of oxygen contains, therefore, rather less than 3 per cent of peroxide

This solution looks like water, but has a peculiar astringent taste. It has no definite smell. It slowly evolves oxygen, so that it must not be kept in perfectly close vessels, since these could thus be readily burst. The decomposition is much less in the cold than in the heat, and is, moreover, very greatly influenced by the presence of other substances. The peroxide can be best preserved in a solution containing a small quantity of some acid or a little spirit of wine.

151. Hydrogen Peroxide as Oxidising Agent.—The ease with which the peroxide decomposes into water and oxygen is also seen in the presence of such substances as can chemically combine with oxygen. Hydrogen peroxide is therefore an *oxidising agent.* Since gaseous oxygen is spontaneously formed from the peroxide, and the reverse reaction does not take place to a measurable extent, we must conclude that the peroxide is a stronger oxidising agent than gaseous oxygen, *i.e.* the peroxide can still give up oxygen to such substances as are not capable of forming compounds with oxygen *gas.* This conclusion is based on the following reasons : -

It can be proved generally that the action of any oxidising agent can, theoretically, be replaced by the action of oxygen gas under an appropriate pressure. The highest pressure of oxygen corresponds to the strongest oxidising agent, and *vice versa.* Imagine this pressure determined for each oxidising agent (which is generally possible by indirect means), we can then arrange these in a series of decreasing pressures, and we can assert that with a higher oxidising agent we can, indeed, prepare every lower one from oxygen and the other component, but not conversely, just as the pressure of oxygen can, spontaneously, only diminish, but not increase   Since oxygen gas can be prepared from hydrogen peroxide, but not hydrogen peroxide from oxygen, the peroxide must be the higher oxidising agent.[1]

These oxidising properties are particularly conspicuous in the case of the pure peroxide. In contact with it lead powder ignites spon-

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[1] In applying this reasoning, it is necessary to know that in the case of an oxidising agent existing in the condition of a solution, its position in the series is variable   It is dependent on the concentration of the solution, and is all the lower the more dilute the solution is made. The same part is played by the pressure of gases, as, indeed follows from what has been said. For solid substances and unmixed liquids, however, the position in the series is fixed and undergoes an appreciable alteration only through change of temperature, which varies from case to case.

153. **Preparation of Pure Hydrogen Peroxide.**—Hydrogen peroxide is much less volatile than water. When, therefore, a solution of the substance is evaporated the water passes off, and a solution, richer in peroxide, remains behind. Although the decomposability of the peroxide rapidly increases with increasing concentration, fairly strong solutions can still be obtained if one starts with very pure material, and carries out the evaporation at a moderate temperature.

Under reduced pressure the concentrated solution can finally be separated into water and almost pure peroxide. For this purpose the parts of a distilling apparatus (p. 111) are connected air-tight together, and after the liquid to be distilled has been introduced the apparatus is exhausted.

The purpose of distillation under reduced pressure is to enable one to accomplish the distillation at a *lower temperature*. Since the vapour pressure of all substances rises with the temperature, and boiling occurs when the vapour pressure has become equal to the external pressure, the substance will boil at a temperature which is all the lower the smaller the external pressure is made.

The lower the temperature, however, the less is, in general, the *amount of decomposition*, since the velocity of this, like that of all chemical processes, rapidly increases with rising temperature. Distillation under reduced pressure, therefore, is employed in all cases where a substance has to be distilled which is not stable at the temperature of its ordinary boiling point.

When a solution rich in peroxide is treated in this manner, whereby the temperature must be kept under 80°, water with a little peroxide first distils over and then almost pure peroxide. The distillate is collected in a separate vessel, and in this way the substance is obtained in a very pure condition. Such a process, depending on the differences of the vapour pressures, is called *fractional distillation*. In chemical practice this method finds very widespread application.

154. **Occurrence.**—Hydrogen peroxide occurs in very small quantities in nature, traces of this substance being contained in rain and snow. Likewise, small quantities of peroxide are produced in many cases of combustion and also in other oxidation processes. There are a number of very delicate reactions used for the detection of such small amounts. These, however, cannot be discussed here, since they presuppose a knowledge of other substances. They will be discussed at a suitable opportunity later (Chaps. XXIX. and XLI.).

155. **Catalysis.**—Since hydrogen peroxide can decompose spontaneously into water and oxygen, a question arises similar to that asked on p. 65 with regard to the combustion of substances in the oxygen of the air: Why, then, does the hydrogen peroxide not decompose? The answer is similar: It does decompose, but with very varying velocity. To illustrate the existing relations by an analogy, one can imagine the

hydrogen peroxide replaced by liquid oxygen contained in a vessel which is not completely closed. The oxygen in this vessel is also not in a permanent condition of equilibrium, but it escapes; still, although it is in communication with a space of lower pressure, its pressure does not fall to the lower value *instantaneously*, but only slowly, and thus with a velocity which depends on the size of the opening and on the amount of friction which takes place in the opening If the opening is very small, it may be a long time before the escape of the oxygen becomes noticeable. Every circumstance which makes the opening more accessible will hasten the lowering of the pressure; every circumstance which makes it less accessible will lengthen the period of the existing condition

In the case of hydrogen peroxide, now, there are, as a matter of fact, very various circumstances known which act in the sense of an enlarging or diminishing of the opening, *i.e.* which change the velocity with which this spontaneous and continual decomposition takes place. Thus, porous and powdered substances greatly accelerate the evolution of oxygen. The action is, however, by no means a purely mechanical one, for different powders of similar fineness have a very different action according to their chemical nature. Pyrolusite, which in like manner also accelerates the perfectly similar decomposition of potassium chlorate when heated (p. 63), is especially effective. By shaking a solution of hydrogen peroxide with pyrolusite in an apparatus which allows of the evolved oxygen being collected and measured, the amount of hydrogen peroxide in the solution can be easily and quickly determined.

On investigating the pyrolusite after the experiment it is found to be unchanged Finely divided platinum, which likewise remains unchanged, acts in a similar manner. Other finely divided metals, such as copper and cadmium, do not appreciably hasten the decomposition.

Such substances which act as pyrolusite and platinum do here, so as to alter the velocity of a chemical process without themselves being changed by the process, have already been mentioned (p. 107). they are called *catalysers*, and the action itself is called *catalytic action.*

* Of the catalysers it can be stated generally, that *they cannot bring about reactions which would not of themselves take place spontaneously if even only with a very small velocity.* If it were the case that a reaction could be brought about by a catalyser in a direction opposite to that which it takes by the action of the participating substances *alone*, one could allow the substances to interact alternately with and without a catalyser, and thereby, time after time, obtain reversed processes. These processes could be used to perform work, and one could thus establish a *perpetuum mobile* of the second kind (p. 136), which is in opposition to experience. Thus it is not to be expected that a catalyser could be found through the action of which oxygen

153. Preparation of Pure Hydro... ...logen peroxide.
peroxide is much less volatile than w... ...entical with the
of the substance is evaporated th... ...ty of a *perpetuum*
richer in peroxide, remains behin... ...
the peroxide rapidly increases wi... ...xide. Approximately
strong solutions can still be obt... ...e, since it readily
material, and carries out the evap... ...The cause of this

Under reduced pressure the ... ...water and oxygen
separated into water and almost ... ...the action perhaps of
the parts of a distilling appar... ...ing portions become
together, and after the liquid ... ...amounts of heat are
apparatus is exhausted. ...advance one another

The purpose of distillation ... ...sion.
to accomplish the distillation at ...ctions take place in
pressure of all substances ... ...For example, when
occurs when the vapour pres... ...and the vapour pressure
pressure, the substance will, b... ...n the reverse manner
lower the smaller the externa... ...sent a *state of equilibrium*
The lower the tempera... ...y state which can be
amount of decomposition, sin... ...the approach to the state
chemical processes, rapidly ... ...ce of slowness.
tillation under reduced p... ...the peroxide the heat
where a substance has t... ...influence of pyrolusite or
temperature of its ordinary ...a thermometer, for the
When a solution rich ... ...ordinary solution, which
by the temperature must ...on sudden decomposition,
peroxide first distils ... ...ent were avoided.
distillate is collected ...n a knowledge of those
substance is obtained ... ...sses is an important task
depending on the diff... ...many general questions.
fractional distillation. ...the amounts of heat given
widespread application ...f energy connected with
154. Occurrence. ...chemical processes are the
quantities in nature, ...ng things, plants as well as
and snow. Likewise, ...life, since, also, the energy
many cases of combustio... ...from chemical sources,—the
are a number of very ...asily seen. We shall here
small amounts The... ...stigations.
presuppose a knowledge ...is a kind of energy. It is
at a suitable opportun... ...produced with especial ease
155. Catalysis. ...any chemical reaction occurs
taneously into water ... ...n general, a different energy
on p. 65 with regard t... ...of the two amounts appears
the air: Why, then, do...
answer is similar. ...centrated solutions. In the case of
To illustrate the exist... ...the spontaneous formation of small

...sult, the production of other forms of energy
...cupped if the energy of the products is smaller
...distances, the temperature of the reacting
...nversely, if the substances are converted into
... energy than the original ones, the energy
...ken in the form of heat from the reacting system,
... this falls. Both cases are possible, but the
...more frequent.
...which the chemical reaction takes place is sur
...unk of water, the heat which is generated passes
..., in the converse case, is taken from it. If the
... is known, and if the change of temperature be
... product of the two numbers gives the quantity
... For the *unit of heat*, or the *calorie*, has been
... the quantity of heat which is necessary to change
... 1 gm. of water 1. If N gm. of water experience
...perature of t, the corresponding quantity of heat is
... to 4·18 Nt joules.
..., however, the quantity of heat developed varies with
... *substances*, and is, indeed, proportional to this.
... in definite numbers, therefore, the quantity of heat
... to definite amounts of substance. For this purpose
... method of procedure is in general use.
... is expressed by a chemical equation, and is imagined
... between as many grams of the different reacting sub-
... numbers of the corresponding combining weights amount
... of any substance whose weight in grams is equal to
... the combining weights contained in the formula, we have
... of the substance (p. 159). In short, therefore, the quan-
... in chemical reactions are calculated for moles of the
... substances.

The Heat of Formation of Water. To give an example
... has just been said, let us consider the development of heat
... in the combination of oxygen and hydrogen. Evidently
... considerable, since it gives rise to such a great elevation of
... perature as the experiments mentioned on p. 103 show.

... experiments which have been performed in this connection
... that in this process 68,400 calories are developed, when one
... 18·02 gm. of water is formed from its elements. An idea
... quantity is obtained on considering that, according to this, more
... a litre of water could be heated from 0 to boiling through
... combustion of 3 gm. of hydrogen.

* This number can be at once used for an interestin
if we imagine the heat which is developed used only fo
...mperature of the aqueous vapour produced by the comb
...tonating gas, the temperature of the flame of the

blowpipe is obtained by dividing the quantity of heat, 68,400 cal., the amount of heat required to raise 18·02 gm. of aqueous vapour degree, or the *thermal capacity* of this amount of vapour. Since round numbers, 9 calories are required to heat 18 gm of water vap 1°, the result of the calculation is that the temperature of the oxy hydrogen flame must be 68,400 9 · 7600°. This number proves, how ever, to be much too high, since measurements have given values whi do not much exceed 2500°.

The cause of this disparity must be sought for in two directi In the first place, the thermal capacity of aqueous vapour has given value only at lower temperatures: at higher temperature becomes greater, and the temperature must therefore become low But then and this is the chief point the combination of oxygen hydrogen to water is not at all complete at higher temperatures, the higher the temperature is, the greater is the portion whi remains uncombined. The combustion, therefore, raises the tempe ture of the flame only to the point where a further elevation wo effect a separation of the water produced into its elements. Furth combustion then takes place only in proportion as heat is withdra by conduction and radiation, and must be replaced by fresh combusti This temperature is then the true temperature of the flame; for t oxyhydrogen flame this is, as already mentioned, about 2500°.

On the basis of the law of the conservation of energy, we can sta in the first place, that the same quantity of heat, 68,400 cal., as w developed in the formation of one mole of water from its element will be again *absorbed* in the *decomposition* of water into its element For if this were not the case, it would be possible, by the alterna formation and decomposition of a given amount of water, to cause t production or the disappearance of any desired amount of energy

The further conclusion can also be drawn, that the same quanti of heat pro mole will always be developed, no matter in what w water is formed from its elements, whether by combustion with flag or by any other process. The correctness of this assertion c also be proved from the law of the conservation of energy. In t case we must only hold to the supposition that no other forms energy appear or disappear

On the other hand, the development of heat must be different, water is produced not from the gaseous elements but from some othe substances which can yield oxygen and hydrogen. And, indeed, t difference must amount to exactly as much as the amount of he developed or absorbed in the conversion of the gaseous elements in the compounds in question. This theorem, also, is based on the la of the conservation of energy.

With reference to the problem before us, the principle of the co servation of energy in its most general application assumes t following form :—

There can, in general, be ascribed to every substance existing in a definite state a definite content of energy, which is proportional to the amount of substance, and which for a mole has a definite value. The absolute amount of this energy is unknown to us, since we cannot in any way abstract from a substance *all* the energy which it contains. We can, however, measure the *differences* of energy between two substances before and after the chemical process, for these are the amounts of energy which are developed or absorbed as heat in the reaction. The energy relations of substances can be represented in the form of equations in which the energies of the single substances are so represented that their differences have definite values.

Thermochemical Equations From this there follows a method of stating the results of such measurements in a manner suitable for calculation. The chemical formula of a substance receives an additional significance that it represents not only the composition but also the *energy content* of the substance. The equation of a chemical process, then, which, apart from this, contains on either side the same elements in equal amounts (p. 148), must be supplemented by the statement of the amount of energy which is necessary to make the values of the energy on both sides also equal. This is the difference of the amounts of energy of the substances before and after the reaction, i.e. the amount of heat developed in the reaction.

For example, to express the change of energy in the formation of water from its elements, in the form of such an equation, we write

$$2H_2 + O_2, \quad 2H_2O + 2 \times 68,400 \text{ cal.,}$$
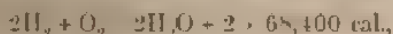
which we read thus The energy of two moles hydrogen and one of oxygen exceeds that of two moles of water by $2 \times 68,400$ cal.; or When oxygen and hydrogen unite to form water, water is produced with an amount of energy equal to 68,400 cal. pro mole of water.

This method of writing allows, in the first place, of the results of measurement being represented in an unambiguous manner. It has the other great advantage that it also makes it possible to calculate heats of reaction of processes which cannot be directly measured. An example of doing this will be given immediately when we come to such an actual case.

As regards the form of these calculations, it has to be further remarked that in future the absolute unit of energy, the *erg* (p. 23), will be used in place of the arbitrary unit of heat, the calorie. Since the *erg* is too small for the accuracy of thermochemical measurements hitherto attained, the kilojoule, kj 10^{10} erg, is used in its place. To turn calories to kilojoules, we have the equation 1 cal. $= 4.184$ kj, or 1 kj 239·1 cal. The equation, therefore, for the formation of water from its elements reads

$$2H_2 + O_2 = 2H_2O + 2 \times 286 \ kj.$$

160. Heat Effects in the Decomposition of Hydrog‍ Peroxide.—The development of heat which accompanies the dec‍ position of hydrogen peroxide into water and oxygen gas (p 162) ‍ be represented in a similar manner.   The result obtained by meas‍ ments is that an amount of heat is developed equal to 97 *kj* ‍ mole of hydrogen peroxide.   We must therefore write

$$2H_2O_2 - 2H_2O + O_2 + 2 \times 97 \, kj.$$
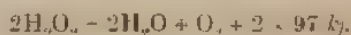
From this there follows, by rearrangement,

$$2H_2O + O_2 \quad 2H_2O_2 - 2 \cdot 97 \, kj.$$

This equation differs strikingly from the former one.   Wherea‍ the previous case the *formation* of the compound was accompanied ‍ a development of heat, the compound containing, therefore, less ener‍ than the components, the opposite is here the case.   One must n‍ therefore, assume that *every* process of combination takes place w‍ evolution of heat : the reverse is also possible, although less freque‍

If we write the two equations

$$2H_2 + O_2 - 2H_2O + 572 \, kj$$
and
$$2H_2O + O_2 \quad 2H_2O_2 \quad 194 \, kj$$
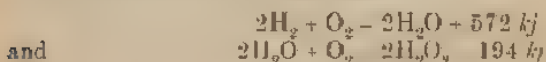
below one another and add, we obtain

$$2H_2 + 2O_2 - 2H_2O_2 + 2 \times 189 \, kj.$$
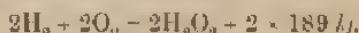
Expressed in words, this equation reads : In the combination ‍ oxygen and hydrogen to form hydrogen peroxide, 189 *kj* are develop‍ for every mole.

In this way we obtain the heat of reaction of a process which c‍ not be carried out in such a way that it can be measured, and whic‍ therefore, cannot be directly investigated.   The justification for t‍ calculation lies in the fact that every formula in a thermochemic‍ equation represents a definite amount of energy, and in the fact t‍ energy magnitudes can be added without limit.   The calculatio‍ therefore, presupposes nothing more than the validity of the law of ‍ conservation of energy.

On subtracting the upper equation from the lower we obtain

$$2H_2O_2 + 2H_2 - 4H_2O + 2 \times 383 \, kj.$$

That is : on the combustion of hydrogen to water by means ‍ hydrogen peroxide, 383 *kj* pro mole of peroxide are evolved.   He‍ again, the heat effect of a reaction has been calculated which cann‍ be subjected to direct measurement.

As can be seen from these calculations, one can, on the basis o‍ few measurements, calculate the heat effect of quite a number

reactions which take place or could take place between the reacting substances. The number of calculations possible increases very rapidly with the number of direct measurements. There is a whole branch of scientific chemistry, known as *thermochemistry*, which has the study of these relations for its object.

These calculations can be most readily reviewed, if for each compound the (positive or negative) heat effect which accompanies or would accompany its formation *from its elements* is calculated. This is called the *heat of formation*. The heat of formation of water is equal to 286 *kj*; that of hydrogen peroxide, 189 *kj*.

In the sequel we shall give the heats of formation of the most important substances so far as they are known; from them there can then be calculated the heat effects of the other reactions in which these substances take part.

CHAPTER IX

161. Formation from Hydrochloric Acid and Oxygen.—
now turn to the study of hydrochloric acid, which was used (p. 86
the preparation of hydrogen.   From those experiments it follo
that hydrogen is one of its constituents.   It contains, besides, anot
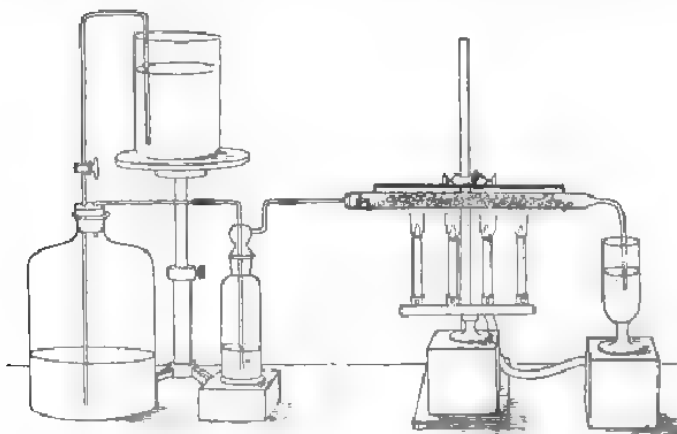
Fig. 61

element called *chlorine*, which in that experiment did not beco
visible because it united with the zinc, for which very reason, inde
hydrogen was formed.

To obtain this other element we must proceed in the reve
manner : to set free the chlorine, we must convert the hydrogen i
a compound which can be separated.   This we can effect by acting
hydrochloric acid with *oxygen*.   If this action took place in the desi
way, hydrochloric acid plus oxygen would pass into water plus chlori
and we should attain our object.

As a matter of fact this process is practicable.   If a current of

... p. 169, where chlorine and water were produced from hydrochloric ... and oxygen, a contradiction seems to be contained in the foregoing ... statement, for in that case exactly the opposite reaction took place, ... chlorine in contact with water formed a more stable system than ... hydrochloric acid and oxygen. The difference lies in the fact that in ... former case we were dealing with *gaseous* hydrogen chloride, but ... with a *dilute aqueous solution* of it. The stability of a compound ... apparently much greater in solution than in the pure state, and ... reactions can, therefore, readily undergo reversal, according ... one or the other condition obtains.

Chlorine Hydrate. The Phase Law. When gaseous ... is passed into ice-cold water—it is best to have some pieces ... floating in the liquid—a greenish crystalline substance soon ... out. This consists of chlorine and water according to the ... $Cl_2 \cdot 8H_2O$, and is called *chlorine hydrate*. Under atmospheric ... this substance is stable only up to $+ 9.6°$; if heated to a ... temperature it decomposes into chlorine, which escapes as a gas, ... water (saturated with chlorine), which remains behind. If the ... be increased, chlorine hydrate can be kept at still higher tem... ... if it be lowered, the temperature of stability of the hydrate ... lower. There corresponds to each temperature, therefore, a ... pressure of the chlorine gas, at which the hydrate can exist.

These relations show the greatest similarity to those existing in ... case of a volatile liquid (p. 122), where the possibility of liquid ... vapour existing side by side is also associated with a definite ... which increases with rising temperature but is independent ... relative or absolute amounts of the two forms. In this case ... the existence of chlorine hydrate in contact with gaseous chlorine ... is regulated only by a relation between pressure and ... and the quantity relations have no influence.

A difference exists here, however, in so far as, in the condition of ... there are present, not *two* phases (p. 131), but *three*, viz. ... hydrate, saturated aqueous solution of chlorine, and gaseous ... This is due to the fact that we are not now dealing with ... equilibrium of a *single* substance, as in the case of water, but with ... substances, water and chlorine. In the same measure as the ... of substances increases, the number of phases which can exist ... also increases.

Just as water along with vapour or along with ice, *i.e.* two phases ... water can exist side by side at *different* temperatures, but three ... water, vapour, and ice, only at *one single* temperature, so in ... present case there can exist *three* phases side by side at different ... and there must be a single point at which *four* phases ... present. Such a point is got when we assume ice as fourth ... As a matter of fact, ice, chlorine hydrate, chlorine water, and ... gas can exist side by side at the temperature $-0.24°$. This

concentrated hydrochloric acid is placed   The evolution of gas takes place in proportion as the acid is allowed to flow to the bleaching powder.

The theory of this process cannot be given till later (Chap. XXIII.); it must suffice here to indicate that we are again dealing with an oxidation of the hydrochloric acid, the hydrogen of this being converted into water.

163. **Properties of Chlorine.** — By these methods a gaseous substance is obtained of a yellowish green colour, which is distinguished by very striking properties from all the gases hitherto described.   It possesses in the highest degree the unpleasant smell we have already
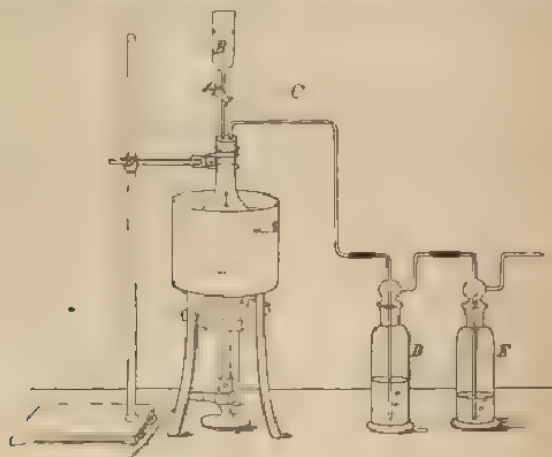
Fig. 62

mentioned, has a corrosive action on the mucous membrane of the mouth and nose, and is therefore very harmful and poisonous   The gas cannot, like oxygen or hydrogen, be collected over water, since it is fairly soluble in that liquid.   In other cases mercury is used for such gases, but it cannot be employed here, since it immediately combines with chlorine.   In order to collect the gas, use is made of its great *density*, if the gas is conducted to the bottom of a dry bottle, it remains at the bottom and gradually displaces the air.   By holding a piece of white paper behind the bottle, it is easy to observe the progress of the filling, the green gas forming a distinct contrast to the colourless air.   When the bottle is filled, it is closed by a ground in stopper, rendered tight with vaseline, and the filling of a fresh bottle is proceeded with

Since some chlorine always escapes into the air during this process, the preparation must be carried out in a good-drawing fume c'   or else in the open air.   Also, while the bottle is being filled

it may be closed by a doubly bored cork through which a supply and a discharge tube pass. By means of a wash bottle with caustic soda, it is then possible to render the escaping gas innocuous.

As is seen from this behaviour, the density of chlorine gas is considerably greater than that of air; its molar weight has been found by measurement to be 71. Chlorine is, therefore, about 2·3 times as heavy as oxygen (M.W. = 32), and 2·5 times as heavy as air.

Chlorine is distinguished from the gases hitherto considered by the fact that it obeys the gas laws with much less exactness. Like all gases of comparatively great density, it exhibits measurable deviations even under ordinary conditions; for with increase of pressure or fall of temperature its density increases *more* than it ought to, according to the gas laws.

Connected with this is the fact that chlorine can be fairly easily condensed to a *liquid*. At 0 a pressure of 3·7 atmospheres is sufficient for this; at room temperature (18) the pressure amounts to 1·5 atmospheres, and the critical temperature is reached only at 146 . Above this temperature chlorine cannot be converted into a liquid by any pressure. The highest pressure just underneath this temperature by which chlorine can still be liquefied, *i.e.* the *critical pressure*, amounts to 94 atm.

These properties, then, make it possible to condense chlorine into steel bottles which have been tested for a considerably higher pressure than the critical pressure, and in which the chlorine can be stored and transported. Although chlorine under ordinary conditions, especially when moist, eagerly combines with almost all metals, carefully dried chlorine shows itself so inactive that there is nothing to prevent its manipulation in metallic vessels. By means of an adjustable cock the gas can be withdrawn from such a holder (Fig. 37, p 105), as desired, and one is thereby spared the very troublesome preparation of the gas when much of it is required.

The peculiar action which water here exhibits is not limited to chlorine; there are very many reactions which take place only in the presence of water with such velocity that the result can be observed in a measurable time. All these must be numbered along with the *catalytic phenomena* (p. 107).

Liquid chlorine has the green-yellow colour of the gas in a much higher degree. It is an oily liquid, of density 1·56.

At lower temperatures chlorine passes into a solid, crystalline substance which exhibits the same green-yellow colour as is shown by chlorine in its other states.

164. **Solubility in Water.**—Chlorine dissolves in water in fairly large amount; under ordinary circumstances one litre of water absorbs about three litres of chlorine. The solution, which has the smell and taste, as well as the corrosive and bleaching properties, of chlorine gas, is called *chlorine water*, and is used for chemical and medical purposes.

... to burn; only
... which green   Th...
... ... ally goes out...
colour ...
the cyli...
appeared...
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and is n...
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chlorine...
is rinsed...
liquid w...
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tion in green plant...
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found on washing out the contents of the bottle with water; these

exhibit exactly the same properties as were shown by the product of

the combustion of hydrogen in chlorine.

The burning of a *wax candle* in chlorine depends on the same

actions. Wax also consists chiefly of hydrogen and carbon (along

with some oxygen). If a burning wax candle be introduced into a

bottle of chlorine, it continues to burn; at the same time, however,

the flame becomes dusky red in colour and emits large quantities of

soot or carbon, since the chlorine cannot, under these conditions,

combine with the carbon. In this case, also, the formation of

hydrogen chloride can be easily demonstrated.

Some of the important technical applications of chlorine depend

on its power of withdrawing hydrogen from substances containing

it, and therefore destroying them, *i.e.* converting them into other

substances.

On the one hand, chlorine is used for *bleaching*. The vegetable

fibres from which textile fabrics and paper are made are generally not

colourless, as it is desirable they should be for use or for being further

treated, but contain natural dyes which must be removed from them.

For this purpose they are treated with chlorine, which removes

hydrogen from the dyes and converts them into other, non-coloured

compounds.

Along with this dehydrogenising action, *oxidation* takes place by

means of the chlorine. This depends on the co-operation of water,

which, as we have already seen, is decomposed by chlorine with

liberation of oxygen. If this process takes place in the presence of

other substances which can form oxygen compounds, these are formed

with special readiness, *i.e.* the substances are oxidised.

On the other hand, chlorine is used for *disinfection* and *sterilising*.

This action also depends on the withdrawal of hydrogen from or the

oxidation experienced by malodorous and other harmful substances

through the agency of chlorine. Especially is chlorine a violent

poison for the small living organisms by whose activity rotting,

putrefaction, and such like, are caused, and which play a part in the

spread of certain diseases. The application of chlorine for such

purposes is, unfortunately, very greatly limited by the fact that it

is also a very harmful substance for the higher organisms, and on

somewhat more prolonged action can give rise to serious symptoms.

7. Composition of Hydrogen Chloride. —The combination of

chlorine with hydrogen is, likewise, subject to the law of Gay Lussac

governing the volume ratios in the interaction between gases (p. 142).

In fact, chlorine and hydrogen combine in *equal* volumes, and the

hydrochloric acid gas formed occupies the same volume as was

previously occupied by the mixed gases. Whereas, therefore, there

was in the formation of water vapour, a diminution from three

volumes to two, we have in the present case a *combination without*

N

change of volume. The molar weight of hydrochloric acid gas therefore obtained as the half of the sum of the molar weights chlorine and hydrogen. This calculation is, in numbers,

$$Cl_2 + H_2 = 2HCl$$
$$70\cdot90 + 2\cdot02 = 2 \times 36\cdot46.$$

One can convince oneself of these relations, both by the deco position of hydrogen chloride, that is, by *analysis*, and by the format of hydrogen chloride from its elements, that is, by *synthesis*.

When an electric current is conducted through hydrochloric by means of two platinum plates, chlorine appears at the one pla and hydrogen at the other The energy which was set free on formation of the hydrogen chloride from chlorine and hydrogen, on the solution of the hydrochloric acid gas in water, is again giv back by the electric current, which therefore makes it possible for two elements to separate in the free state The details of this proc will later form the subject of exhaustive consideration ; at this poi we rest satisfied with the result that the hydrochloric acid is deco posed by the electric current, and that its elements are evolv separately.

This experiment is performed in the apparatus shown in Fig on p 141. On starting the process by passing the electric curre after the apparatus has been filled with strong hydrochloric acid, is at first seen to be evolved only at one electrode ; this gas hydrogen. At the other electrode there is only a yellow gre coloration produced, because the chlorine evolved dissolves in th hydrochloric acid. Gradually this becomes saturated with chlorin and gas is evolved regularly at both plates, or "electrodes"

After the first portions of gas have been allowed to escape, opening the taps, it is easy to satisfy oneself that the two limbs of th apparatus become simultaneously filled with equal volumes of gas an that, as a matter of fact, therefore, equal volumes of the two gases a produced in the decomposition of hydrochloric acid.

That one of the gases is hydrogen is shown by the fact that burns with a blue flame in the air. The other gas can be recognise as chlorine, even by its colour ; the smell and the bleaching action a piece of litmus paper confirm this.

173. Formation of Hydrogen Chloride from its Elements.— If, on the other hand, a mixture of equal volumes of chlorine and hydrogen is prepared, it can be ignited by an electric spark in the same way as detonating gas, and is completely converted, with explosion, into hydrochloric acid. In this case, however, there are some remarkable phenomena to be observed

It is not only by rise of temperature that a mixture of equal volumes of chlorine and hydrogen, which, on account of the similarity mentioned, is called *chlorine detonating gas*, passes into hydroge

is found in washing out the contents of the bottle with water; these exhibit exactly the same properties as were shown by the product of the combination of hydrogen and chlorine.

The burning of a wax candle in chlorine depends on the same relations. Wax also contains plenty of hydrogen and carbon along with some oxygen. If a burning wax candle is introduced into a bottle of chlorine, it continues to burn, at the same time however the flame becomes fairly red in colour and emits large quantities of soot or carbon, since the chlorine cannot, under these conditions, combine with the carbon. In this case, also the formation of hydrogen chloride can be easily demonstrated.

Some of the important technical applications of chlorine depend on its power of withdrawing hydrogen from substances containing it, and thereby destroying them, or converting them into other substances.

On the one hand chlorine is used for bleaching. The vegetable fibres from which textile fabrics and paper are made are generally not colourless, as it is desirable they should be for use or for being further dyed; but contain natural dyes which must be removed from them. For this purpose they are treated with chlorine, which withdraws hydrogen from the dyes and converts them into other less-coloured compounds.

Along with this decolourising action, another action takes place by means of the chlorine. This depends on the evaporation of water which, as we have already seen, is decomposed by chlorine with elimination of oxygen. If this process takes place in the presence of other substances which can form oxides, these are formed with special readiness, or the substances are oxidised.

On the other hand chlorine is used for disinfection and deodorising. This action also depends on the withdrawal of hydrogen from or the oxidation experienced by malodorous and other harmful substances through the agency of chlorine. Especially is chlorine a violent poison for the small living organisms in whose activity rotting, putrefaction, and so forth are caused and which play a part in the spread of certain diseases. The application of chlorine for such purposes is undoubtedly very greatly aided by the fact that it is also a very harmful substance for the higher organisms, and in somewhat more prolonged action can give rise to serious symptoms.

172. Composition of Hydrogen Chloride. The combination of chlorine with hydrogen is likewise subject to the law of Gay Lussac regarding the volume ratios of the interaction between gases (p. 141). In fact, chlorine and hydrogen combine in equal volumes, and the hydrochloric acid gas formed occupies the same volume as was previously occupied by the mixed gases. Whereas, therefore, there was, in the formation of water vapour, a diminution from three volumes to two, we have in the present case a combination of

acid is decomposed by the electric current in the vessel A (Fig.
which is furnished with two electrodes of carbon (thin arc li
carbons), or of platinum   Under these conditions the gases produ
immediately mix and, after the evolution has been going on for a h
or a whole hour, in the right proportions.   In the bulbs which
blown on the delivery tube, there are a few drops of water, to free
gases from the hydrochloric acid which they carry over.   Attached
the delivery tube is a series of glass bulbs blown out of thin glass
connected by thin-walled capillaries ; they may be 4 to 6 cm.
diameter.   These are filled with the explosive mixture by displ
ment.   Since this is heavier than air, the row of bulbs is placed in
upright position and the gas passed in at the foot.   All this must
done in a weak light, with exclusion of daylight ; for this purpose

Fig. 63
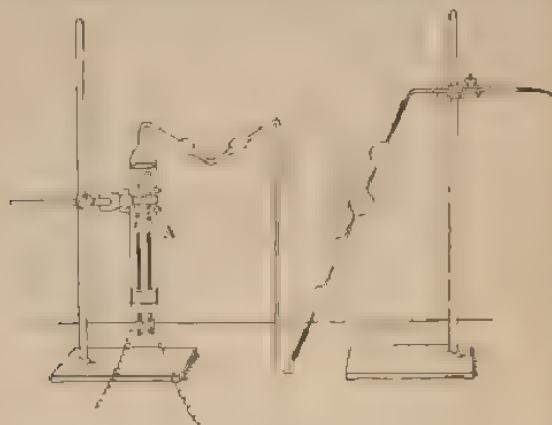
light is most conveniently supplied by a lamp with yellow cylinde
such as is used for photographic purposes.   After the gas has bee
passing for at least half an hour, precautions being taken to carry off th
excess, the two ends of the row of bulbs are closed, for the time being
with wax ; one then proceeds to melt off the bulbs from one another.

Although the chlorine detonating gas can be caused to explode by
heat, the capillaries can, without danger, be softened in a small ga
flame and closed by drawing out.   The gas which is directly heated
burns, certainly, to hydrochloric acid, but the combustion does no
pass into the bulbs, because the heat which is developed is taken up
by the glass walls of the tube.

With the bulbs of chlorine detonating gas prepared in this way
the experiments described can also be carried out   the explosion o
these is unattended with risk, since the light glass splinters can scarcel
do any damage.   Instead of sunlight, burning magnesium can be use
to bring about the explosion · either magnesium powder is placed in

glass tube 1 cm. wide and blown into a flame, or a lamp is employed such
as is used in taking flash-light photographs. In both cases the bulbs
with the explosive mixture must be placed very close to the flame

175. **Photochemical Actions**. It follows from the experiments
described, that the action of light on the chlorine detonating gas,
similarly to that on chlorine water (p. 172), consists in increasing the
velocity of combination of the two components. It has been repeatedly
explained that there is reason to suppose that in every system in which
a chemical process can take place, that process really does take place,
although often only with an immeasurably small velocity. In the case
of the chlorine detonating gas, also, we may make such an assumption,
and the action of light consists in increasing this immeasurably small
velocity to a measurable one

In fact, it has been shown by appropriate investigations, that the
velocity of transformation of the chlorine detonating gas into hydro-
chloric acid is proportional to the strength of the light acting.

" The manner of this action is still somewhat obscure. We must
by no means assume that the energy of the light is expended in bring-
ing about the reaction. No energy is consumed in the combination of
the gases; on the contrary, a fairly large amount of energy is set free,
as follows from the phenomena of explosion, and the spontaneous
transmission of the combustion through a tube at the end of which
it is initiated. From the observation that completely dry chlorine
detonating gas is scarcely sensitive to light, combined with some other
facts, it becomes probable that we are dealing here with a rather
complicated process which takes place with the co-operation of the
elements of water.

176. **Hydrochloric Acid.**—*Hydrochloric acid* is met with in com-
merce as a liquid like water, which, in the pure state, is colourless ;
the crude hydrochloric acid, however, is generally coloured yellow
through contamination with iron. This is not the pure compound
hydrogen chloride, but a solution of it in water. Pure hydrogen
chloride is a gas, and as such is difficult to employ and to transport.
A solution of it in water, containing rather more than a third of its
weight of hydrogen chloride, is therefore used. Solutions containing
this amount or more of hydrogen chloride *fume* in the air, gas being
given off ; solutions containing less than 20 per cent of hydrogen
chloride no longer fume at the room temperature.

In order to obtain pure hydrogen chloride gas from its solution,
commercial hydrochloric acid, it is necessary to withdraw the water
from the latter We have already learned that concentrated *sulphuric
acid* can be used for such purposes. Accordingly, our apparatus con
sists of a bottle through the cork of which pass a dropping funnel and
delivery tube. The tube of the dropping funnel, which is filled wit
fuming hydrochloric acid, is drawn out to a narrow point and reach
to the bottom of the flask. If the tap be opened and the hydrochlor

acid allowed to pass slowly into the sulphuric acid, the water is [...]
up by the latter and the hydrogen chloride escapes as a gas.

The upper part of the generating flask does not become color[...]
hydrogen chloride is, therefore, colourless. It cannot be collected[...]
water, nor can it be collected well by displacement, since it is [...]
slightly heavier than air. It can, however, be collected over mer[...]
since this is not attacked by hydrogen chloride when both subst[...]
are pure.

* The use of mercury for collecting such gases as are readily [...]
solved by water is due to Priestley (1780), and was, at the tim[...]
important invention, since it led directly to the knowledge of qu[...]
number of gases which are dissolved by water, and of which, there[...]
one could previously know nothing. The mercury trough whi[...]
used in such operations is generally made of porcelain, and of so[...]
form that the quantity of this rather expensive metal required to [...]
it is as small as possible.

177. Properties of Hydrogen Chloride. -Hydrogen chlori[...]
a colourless gas, the density of which amounts to 36.5, correspon[...]
to the formula HCl. It is, therefore, a little heavier than air. [...]
pressure and cold, it can be converted into a liquid; at $-11[...]$
solidifies. The liquid boils under atmospheric pressure at $-80°$[...]
pressure at 0 amounts to 2.8 atm.

Liquid hydrogen chloride is a colourless, rather indifferent liq[...]
exhibiting little of the chemical reactivity which can be observe[...]
the case of its aqueous solution. The liquid neither acts on me[...]
nor reddens litmus, nor, when water is carefully excluded, do[...]
show any of the other properties of acids. This remarkable con[...]
to the behaviour of the aqueous solution has great significance[...]
will be explained later (p. 184).

Of the other properties of hydrogen chloride the most strikin[...]

its great solubility in water. At [...]
temperature, one volume of water ab[...]
450 volumes of the gas. By the abs[...]
tion, a large quantity of heat is devel[...]
which points to a reaction between [...]
water and the hydrogen chloride [...]
This reaction is of a special kind, [...]
will be discussed more fully at a [...]
point.

The great solubility of hydr[...]
chloride in water can be shown by blo[...]
a little water up through the mercur[...]
the gas collected in a cylinder, by m[...]
of a pipette bent at the lower end (Fig.[...]
The mercury immediately ascends an[...]
the gas is pure, again fills the cylinder. There generally remains,[...]

..., a bubble of air unabsorbed, since it is very difficult to remove ... last traces of foreign gases.

The water which was added has been converted, by the absorption ... the hydrogen chloride, into *hydrochloric acid* If a piece of metallic ...gnesium be introduced under the mercury and allowed to pass up ... the hydrochloric acid, it decomposes this, combining with the ...rine and liberating the hydrogen. When the evolution of gas has ...ased, it is easy to convince oneself that the gas is hydrogen and that ... volume is half that occupied by the hydrogen chloride gas.[1]

178 Absorption of Hydrogen Chloride by Water. In pass ... hydrogen chloride in comparatively large quantity into water for

... purpose of preparing
...-eous hydrochloric acid,
... precautions must be
... ted on account of the
... -ce of the absorption
... apparatus used for this
... -pose is shown in Fig
... The hydrogen chloride
... generated in *A*, *B*
... empty wash bottle,
... a wash bottle half
... with water. The two
... bottles are connected
... opposed to one another,
... at to *B* the gas enters
... -ugh the short and
... ... through the long
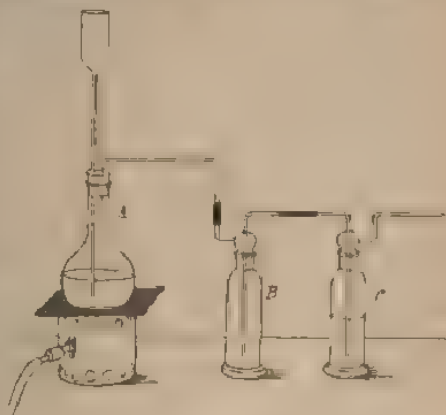
... *C*, in the reverse manner, receives the gas through the long
... When the gas is evolved, it first fills the empty bottle *B*, and
... passes over into *C*, where it is absorbed by the water; the
... ... air escapes through the short tube. If, now, for any reason,
... ... -tion of gas should cease, the water would, if the bottle *B*
... not there, pass back into the generating flask *A*, on account
... the absorption of the gas; by the action of the water
... ... concentrated sulphuric acid, an explosion might result,
... in any case, the experiment would be spoiled The bottle
... ... against this contingency If regurgitation should occur,
... ... cannot get farther than *B*, and if the pressure in *A* is further

... the success of the experiment, the apparatus must previously be carefully ... ..., the volume of the hydrogen chloride, on account of its great ... ... appears too small Also, one must not confine the gas under the ... ... the measurement of the experiment. This is most simply accomplished ... ... always under mercury, placing it in a ... vessel of water, and sinking ... ... of the water outside and inside is the same It is here presupposed ... ... -ering the hydrogen chloride over mercury, that gas also was under atmos- ...

reduced, air passes from *C* through the liquid in *B*.   When th
pressure in *A* again rises, the liquid is first forced over from *B* in
C again, and the absorption goes on regularly.

Besides the one described, there are many other safety arrang
ments to prevent the liquid passing back into the generator   One
the simplest of these consists in inserting an open funnel tube in th
cork of the generator itself (Fig. 67).   It will be easy for the read
himself to work out the action of this in the case of diminish
pressure.

When somewhat larger quantities of hydrogen chloride are di
solved in water, the temperature of the solution rises to an undesirab
height, owing to the heat developed in the process.   The solution
therefore cooled by placing the bottle in cold water or surrounding i
with ice.

In the commercial preparation of hydrochloric acid, the hydroge
chloride is, of course, not prepared by the method employed by us.
It is obtained by the action of sulphuric acid on common salt, accord-
ing to a chemical reaction, the theory of which cannot be developed till
later (Chap. XII.).

179. **Hydrogen Chloride and Water.**—Most gases dissolve in
water to a much less extent than hydrogen chloride, and the absorp-
tion follows a law discovered by Henry, which states that the amount
dissolved is proportional to the pressure.   In the case of hydrochloric
acid, this law is not even approximately fulfilled ; on the contrary, the
greater portion of the gas is absorbed independently of the pressure,
and an increase of pressure effects only a small increase in the amount
dissolved.

This behaviour points to the fact that in the case of the absorp-
tion of hydrogen chloride a special chemical process also takes part
This process consists *in the elements of hydrogen chloride passing, in aqueous
solution, into another condition.*   It is very remarkable that *anhydrous* liquid
hydrogen chloride does not exhibit the properties of an acid (p. 182),
although it contains the elements of one.   This is due to the fact that
the characteristic properties of acids are not exhibited by the com-
ponents of hydrogen chloride until this is converted, through solution
in water, into the other condition

When, therefore, hydrogen chloride is dissolved in water, two pro-
cesses occur   One portion of the acid, which is all the greater the
more dilute the solution, passes into the new condition ; another
portion dissolves unchanged as hydrogen chloride.   The first portion
does not follow Henry's law of the absorption of gases, but only the
second.   For this reason, the amount absorbed increases more slowly
than the pressure.

There is a further remarkable phenomenon connected with this
Hydrogen chloride, in the pure state, boils at - 80 under atmospheric
pressure ; water boils at + 100 .   One would suppose, therefore, that

points of aqueous solutions of hydrochloric acid would lie
...ese two temperatures. This, however, is the case only for
...ntrated solutions ; more dilute solutions, on the other hand,
...lower temperature than water, so that by the addition of
...olatile substance to water, the volatility is not increased but

...ation between composition and boiling point is represented
...re (Fig. 68), in which the percentage content of hydrogen
...measured on
...tal axis, and
...points under
...pressure on
...l. As can
...the curve
...maximum at
...esponding to
...tion, and all
...ixtures boil
...the 20

...t causes the
...behaviour on
...We pre-
...on distilla-
...mposition of
...ean evidently
...y in such a
...the boiling
...for the more
...the lower
...ortion, must
...first, and the

Fig. 68.

...st therefore, necessarily, boil higher than the original
...If now the strength of the acid solution is below 20%,
...ng, more dilute acid must distil over, and a stronger, higher
...remains behind. This continues until the residue contains
...drogen chloride. An acid of this strength cannot leave a
...ng residue, for it is itself the highest boiling mixture; it
...efore, distil over unchanged, and this has been shown by
...to be the case
...ely, if one starts with an acid stronger than 20°, a still
...d must distil over, for the weaker acid has the higher boil-
...and therefore remains behind. But this separation, also,
...arried on indefinitely, for when the strength of the solution
...no acid of higher boiling point can be formed, because
...be such, and the liquid must distil over unchanged).
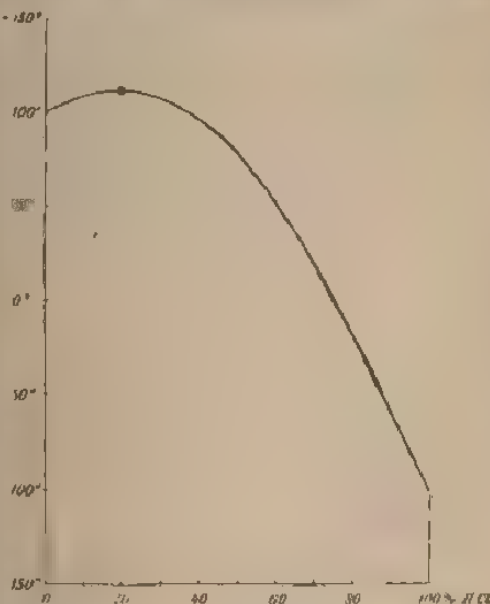
... with an acid of *any* concentration ; on ... ... at the last an acid of 20 , and a ... ...dilute or more concentrated acid will be ... ...with an acid containing less or more ...

... ...been made of regarding this constant boiling ... ...compound. It is not one, for the com ... ...boiling acid is dependent on the pressure ... ...is carried out. Under 2 3 atm., the ... ...under 0·066 atm., 23 ., of acid.

... on the basis of what has been said above, we ... ...theorem that *every* solution, the boiling point of ... ...of the neighbouring solutions on either side ... ...constant composition. By quite similar reasoning ... ...oneself that solutions, also, the boiling point of ... ...of the neighbouring solutions on either side ... ...distillation. In this case, however, the solution ... ...composition appears not in the residue but in the

... ...ions which have been described for hydrochloric ... ...tion of a phenomenon which appears in a striking ... ... hydrogen chloride *gas*, and which is also noticeable ... ...concentrated hydrochloric acid, viz., the *fuming* of this ... It is known that hot water fumes or forms a mist ... ...as a result of its higher temperature, it gives ... ...vapour than can remain in the gaseous state at the ... ...air. Water, however, of the temperature of the ... ...form a mist, for it cannot possibly give off more ... ...be contained in the vapour form in the air Con ... ...chloric acid, however, fumes even without being

... ...of this is that the evaporating hydrogen chloride ... ...vapour in the air, with which it forms a liquid the ... ...of which is much smaller than that of the concen ... ...This solution will, therefore, be precipitated in the ... ... Dilute acid does not fume, for the reason that to ... ...form a less volatile solution with the water vapour in ... ...they contain more water than the difficultly volatile 20 ... ...other hand, the concentrated acid fumes only in *moist* ... ...however concentrated, be placed in a bottle the interior ... ...dried with sulphuric acid, no trace of fumes or mist

... ...these considerations we may conclude that every substance ... ...with water a solution (or compound) of considerably ... ...point, must fume in moist air, whereas this cannot ... ...substances which do not have that property. We shall

he sequel have frequent opportunity of applying and confirming theorems

Properties of Acids.—Hydrochloric acid, or the aqueous ... of hydrogen chloride, is a strong acid. In the name *acid* there ...med up a whole series of properties possessed in common by ...tances of different composition. Of these properties the longest ... is the *acid taste*, which, as we know, is possessed by very ...at substances. A second property shown by all substances with ... taste, is the power of *reddening* the colouring-matter *litmus* ... A third common property is that of *evolving hydrogen* when ...t into contact with certain metals, such as zinc or magnesium. ... last is, for us, the most important property of all. One can ... whether it is a property of all acid substances by bringing acid ... of all kinds, such as vinegar, acid fruit-juices, dilute hydro... acid or sulphuric acid, a solution of citric acid, etc., in contact ... magnesium powder. In all cases, a more or less vigorous evolu... ... takes place, and on testing the gas, it is found to be ... gen

If we introduce the name *acid* for the substances possessing these ...ties, we can say that *all acids contain hydrogen, which they* ... *the action of magnesium* The objection might be raised, ... the hydrogen comes from the water in which all the acids were ... with regard to hydrochloric acid, however, we already know ... contains hydrogen, and the same has been proved by chemical ... with regard to the others. On the other hand, water does ...ppreciably act on magnesium at room temperature.

The properties we have just described are not possessed by all ... compounds, they are wanting in the case of water, and also ... case of spirit of wine, petroleum, stearin, etc. It is easy to ... oneself that these substances contain hydrogen, by setting them ... and holding over the flame a clean, dry glass; it is immediately ...ed with a dew of water drops. The hydrogen of the acids, there ... must also be in the special condition mentioned on p. 184, by ... which it acquires properties belonging only to the acids. ... special relations we shall immediately explain

Acids and Bases.—The properties which we have employed ... identification of acids disappear when *caustic soda* (p. 154) is ... the acid liquids. This is seen most clearly in the case of the ... change with litmus. Dilute hydrochloric acid is coloured red ... drop of litmus solution. If a solution of caustic soda is now ... added to this, the colour at first remains unchanged, then ...aches, which disappear on stirring, are seen in the liquid where ... soda drops, and finally, the whole liquid suddenly becomes ... By working carefully, it is easy to recognise that the blue ... is produced by a single drop of the caustic soda solution. .

At the same time, all the other properties of the acids have disappeared.

... ... acid and does not evolve hydrogen with
... ... Similar experiments can be performed with all

... ... must therefore have taken place by the inter
... ... and caustic soda, the product of which is
... ... the liquid.   A residue is obtained which, in
... ... to be common salt.

... ... common salt consists of *chlorine* and *sodium*
... ... and hydrochloric acid yield common salt, the
... ... ained in them must have been converted into
... ... these other substances are hydrogen from the
... ... and oxygen plus hydrogen or hydroxyl from the
... ... makes up, however, the composition of *water*,
... ... the second product formed by the action of
... ... caustic soda.

... ... seen more clearly when the reaction is expressed

$$NaOH + HCl = NaCl + H_2O.$$

... ... water can likewise be proved by experiment.   If dry
... ... gas is passed over some pieces of caustic soda, water
... ... with great evolution of heat, and can be condensed
... ... long action, common salt remains as the residue.

... ... other substances which, like caustic soda, neutralise
... ... acids, giving rise to new substances accompanied by
... ... water   So far as they are soluble in water, they can
... ... by the fact that they restore the blue colour to
... ... been made red by acids, and withdraw from the
... ... of evolving hydrogen with magnesium or other
... ... are the same substances as we previously (p. 155)
... ... being compounds of metals with hydroxyl, and which

... ... *base* (foundation) is due to the fact that these sub-
... ... the *non volatile* constituent of salts, whereas most of
... ... more or less easily expelled by heating.   That portion
... ... stable to heat was formerly regarded as the more
... ... was called the foundation or base.

Combining Proportions between Acids and Bases.—
... ... which takes place between bases and acids, and which gives
... ... formation of a salt along with water, presupposes a per
... ... ratio between the amounts of each.   If we add a base
... ... much of the hydrogen will disappear as is necessary for
... ... of water with the hydroxyl, viz., 1·01 gm. hydrogen to
... ... hydroxyl.   So long as *hydrogen* is in excess, the liquid will
... ... reaction, for this is not interfered with by the presence
... ... substances.   By continued addition of the base, a point

st be reached when all the hydrogen has disappeared, and
excess of the base. Such a liquid will therefore exhibit
us neither of acids nor of bases; it will, for example, colour
ther blue nor red, but will leave its purple colour unchanged.
uid is called *neutral*. This property is possessed by water
solutions of most of the salts. For example, common salt
tral solutions.

can be made of these phenomena for many purposes. If it
ion of forming salts from acids and bases, litmus is used, best
paper, to determine if the components have been employed
per proportions; so long as blue litmus paper is coloured
is too little base; if red is coloured blue, there is too little

mus paper can also be used to show whether a salt is free
mination with acid or base.

Reciprocal Estimation of Acids and Bases. — The
rtant application of these phenomena, however, is to the
ion of the quantity or the concentration of acids and bases.
e solution of caustic soda be always used, the amount of it
to neutralise different solutions of an acid will be *proportional*
ities of the acid.

method of determination based on this is carried out as

The solution of caustic
ontained in a tube of
diameter, graduated
of etched lines into
imetres and fractions
and closed at the
l by a tap. For
rposes a piece of
ubing can be used,
pressed together by
pinch cock; further,
ake of the better
of the outflow, a
ss tube, drawn out
t, is inserted in the
. This apparatus is
tte (Fig. 69).

termine the amount
n any given sample,
ilute hydrochloric
p of litmus solution
the burette is filled
ro mark of the graduation with caustic soda solution, care
ken that no air bubbles are present in the tap and the
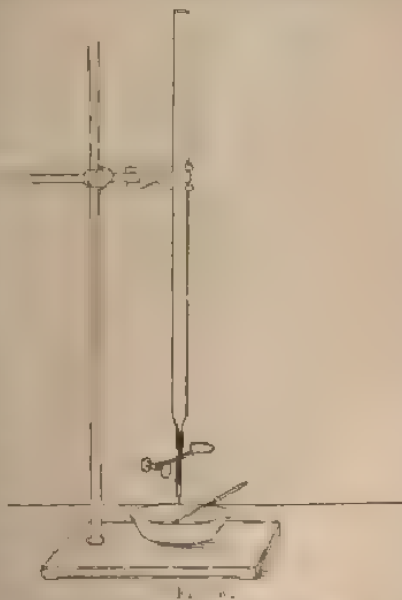
outflow jet.   The caustic soda is then allowed to flow
acid until the red colour of this suddenly changes to blu
approach of this point can be seen, since, shortly before it is
blue patches, which at first disappear on stirring, are forme
the caustic soda flows into the acid.   The caustic soda is the
drop by drop, and the amount by which the blue coloration
duced can be obtained to within one drop.   The amount
solution used can be read on the graduation of the burette,
that the amount of acid can be calculated.

For this purpose the strength of the caustic soda solution
known.   As a rule, it is prepared so as to contain one eq
weight, equal to 40·06 gm of caustic soda, in one litre of
Such a solution is called *normal*.   Exactly a litre of this sol
required to neutralise as much acid as contains 1·01 gm. by
for example, 36·46 gm hydrogen chloride.   If n cc. of
solution have been used, there must have been $\dfrac{n \cdot 36\cdot46}{1000}$
$n \cdot 0\cdot03646$ gm hydrogen chloride present.

As a rule, it is not a matter of determining the absolute a
acid, but the *concentration* of given solutions.   To ascertain
acid contained in a definite amount of the solution has to
mined   This amount can be weighed out, but it is m
venient to measure it volumetrically   For this
apparatus called *pipettes* are used (Fig 70).   They c
narrow glass tubes, widened in the middle, and are
such a size as to contain, up to a mark on the neck,
number of cube centimetres.   To fill them, the liquid i
up past the mark ; they are then closed by the forefin
the liquid is allowed to run out exactly to the mark,
contents are then emptied into the vessel in which the
nation is to be made

By the operation of neutralisation from a bu
"titration," the amount of acid in the measured v
ascertained, and from that it is easy to calculate the
contained in unit volume, that is, the concentration.
example, we have measured off s cc. of acid with the
and have used n cc of normal soda solution, the conce

Fig 70.
is equal to $n s$ combining weights in a litre, or
in a cubic centimetre   If M is the combining weight, M
is the amount of the substance in grams in a cubic centimetre.

184 **Volumetric Analysis**. This method of chemical
ment by means of liquids of known content, is called
analysis, and the operation, *titration*   The method is not li
the reciprocal determination of acids and bases , on the
there are a number of other reactions which take place in
solution accompanied by change of colour or other well

phenomena.   On all such reactions methods of volumetric analysis can be based

Solutions which in one litre contain one combining weight of the active substance in grams, are called *normal*.[1] If they contain only a tenth of this amount, they are called deci-normal (n 10), and so on. To prepare the solutions, the requisite quantities of the substances are weighed out and introduced into flasks of the desired capacity. This volume is exactly marked off by a ring on the neck of the flask (Fig. 71). Such vessels are called *measuring flasks*.

Lastly, *measuring cylinders* (Fig 72) are used in volumetric analysis where comparatively large quantities of liquid have to be measured, the volume of which is not given in round numbers. They consist of cylinders set on a foot and furnished with etched graduation marks.

Fig. 71

185. **Ions.**—It has already been several times pointed out that the *hydrogen of acids* behaves in an essentially different manner from the hydrogen of other compounds. It always gives the same reactions, independently of what the other components of the acids may be; for example, it is always displaceable by magnesium and other metals, and to it the common property of acids, that of reddening litmus, is due.

In the same way, the *hydroxyl of bases* always shows concordant properties. It is the cause of the reddened litmus being changed to blue and on it depends the formation of new compounds, *salts*, with the simultaneous production of water, under the action of acids. These properties belong only to the hydroxyl of bases, and are not shown by other hydroxyl compounds which are known in large numbers.

A similar independence of the chemical properties of the compounds possessing them is shown in the case of the salts. The following example will make this clear.

If a small quantity of a soluble *silver* salt, *e.g.* silver nitrate or lunar caustic (p 58), is added to a dilute solution of hydrochloric acid, a white precipitate is immediately produced which, on shaking, becomes flocculent and looks like curdled milk, and which has the property of becoming grey when exposed to light.

If, now, different salts are prepared from hydrochloric acid, either by decomposing the acid with metals or saturating it with bases, *all these salts have the same property*, they all give the precipitate with silver salts, and the metal with which the hydrochloric acid has formed the salt is without influence on the production and nature of the precipitate.

In Great Britain it is customary to define a normal solution as one which in 1 litre the *hydrogen equivalent* of the active agent weighed in grams. T

circuit in contact with the electrolytes are called *electrodes*. We have several times, previously, made use of the phenomena of electrolysis for the purpose of separating and identifying the components of an electrolyte in a simple manner (pp. 140 and 178).

The exhaustive investigation of the substances which possess the property of electrolytes has shown that they are ionic compounds or salts, and only these. *Salts are electrolytes*, i.e. the property of conducting the electric current, with decomposition, is inseparable from the presence of independently reacting components or ions.

Thus water, for example, is not an electrolyte.[1] We can convince ourselves of this fact by means of the decomposition apparatus shown in Fig. 73. This consists of a beaker filled with the liquid to be investigated, to which the current from an electric cell (an accumulator) is led by two electrodes of platinum. This metal is chosen because it is
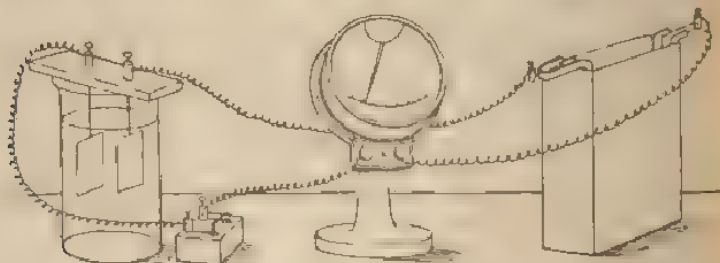
Fig. 73.

not attacked by the substances which separate out at the electrodes; most of the other metals are not so resistant. To recognise the passage of the current any current indicator, e.g. an electric bell, can be used. A measurement of the current can at the same time be effected by using as indicator a current meter or ampere-meter, which must indicate hundredths of an ampere.

If the vessel is filled with pure water and the circuit closed, the instrument shows no deflection. On adding a little hydrochloric acid, caustic soda, or common salt, to the liquid, a current forthwith passes, the measuring instrument shows a deflection, and gas is evolved at the electrodes.

187. Anions and Cations.—The more exact investigation of the processes which take place in electrolytes under the influence of the current, has yielded the following results.

The *hydrogen* of the acids always separates at the so-called *negative*

---

[1] Speaking strictly, water is certainly an electrolyte, but it possesses this property to an exceedingly small degree. A cube of water with a section of 1 sq. cm. conducts worse than a column of mercury a million kilometres in length, having a section of 1 sq. cm. At a later stage we shall discuss the properties of water which depend on this small conductivity; we leave them out of account here, in order not to complicate the description.

electrode, or the electrode at which the positive current leaves the electrolyte to pass into the metallic conductor. At the same electrode, the metals of the salts appear. This is readily seen if a silver or copper salt be decomposed in the apparatus described; the former metal forms long needle shaped crystals, the latter covers the electrode with a red coating which exhibits the colour of pure copper.

The ions which wander to the negative electrode and separate out there, are called *cations*,[1] and the electrode is called the *cathode*. Hydrogen is the cation of acids; the metals are the cations of the salts and bases.

At the second electrode chlorine appears in the decomposition of the chloric acid and of the salt like metallic chlorides, and can be identified by its colour and its reactions. The ions which move in the opposite direction to the cations are called *anions*. Chlorine is therefore the anion of hydrochloric acid and of the metallic chlorides. The electrode at which the anions separate is called the *anode*.

For the sake of shortness, we have here, in the first place, designed that which separates at the electrodes by the name of the ions. It must however, not be forgotten that the ions preserve their ionic state only in the solutions. At the electrodes, the electric current passes through the metallic conductors, while the ions are eliminated at these points. In this process the ions are converted at the electrodes into the allotropic or isomeric forms (p. 193), and this goes hand in hand with a change in their electrical relations, which we shall consider.

The First Law of Faraday. —By a series of careful measurements Faraday, in 1833, established the law that the amounts of the substances which separate at the electrodes are strictly proportional to the quantity of the electric current which was passed through the electrolyte. From this the idea arises that the passage of the electricity through the electrolyte is united with the simultaneous movement of the ions, so that no current at all can pass if it is not carried by the ions.

In accordance with the relation which we have just stated to exist between the direction of the current and the chemical nature of the substances which separate out, the cations (hydrogen and metals in the above case), are to be regarded as the carriers of quantities of *positive* electricity, whereas chlorine, as ion, transports *negative* electricity. At the electrodes, the current leaves the ions, being propagated in the metallic conductor without the simultaneous movement of substance.

We can therefore make the distinction between ions and the elements or compounds produced from them, clear to ourselves by regarding the ions as electrically charged substances, whereas the substances in the ordinary state are non-electrical. This view is a

[1] The name is intended to express that these ions wander downwards in the direction of the current.

good representation of the actual relations, and it may be employed without entering more fully into the way in which the electrical charge on the ions is united with the substances. This new conception is in harmony with the criterion mentioned above (p. 193), that the ions differ from the non-ions of like composition in their *energy content*, for an electrically charged body has necessarily, in consequence of its charge, a different content of energy from an uncharged one.

189. **Electrical Units.**—To enable the connection between the chemical and electrical phenomena to be clearly expressed, some of the fundamental laws of electricity must be here recalled.

By various means, such as galvanic cells, dynamos, thermopiles, etc., a process can be brought about in conductors of electricity which is called an *electric current*. By it, all kinds of work, both mechanical effects as well as chemical decompositions, can be performed at any point of the conductor, and heat or other forms of energy produced. The electric current, therefore, represents a special *form of energy*.

The current can be measured by applying the law of Faraday which has just been enunciated, according to which the *amount of electricity* passing through an electrolyte is proportional to the *amount of substance* which is at the same time decomposed. If, therefore, an electrolytic cell be introduced in the circuit, the quantity of gas evolved, for example, is a measure of the amount of electricity which has passed through. By *strength of current* there is understood the quantity of electricity which has passed, divided by the *time required*, or, the amount which passes in unit time. The strength of the current can therefore be measured by the amount of gas evolved in unit time.

The unit of quantity of electricity is called the *coulomb*; it has been determined in a manner which cannot be explained here. To reduce the coulomb to a measure with which we are familiar, we make use of the fact that for the evolution of 1·01 gm. hydrogen, 96,540 coulombs must pass through the electrolyte.

A current which in each second conveys one coulomb through the conductor, is called an *ampere*. In order, therefore, that a current of one ampere shall liberate 1·01 gm. hydrogen, it must flow for 96,540 seconds, or 26 hours and 49 minutes, through the electrolyte.

Very weak currents are measured in milliamperes or thousandths of an ampere.

A current is not determined by the number of amperes alone, for currents of the same number of amperes can produce very different effects, according to the nature of the conductor. The relations here are the same as in the case of a stream of water which can, with the same amount of water, perform various amounts of work, according to the pressure or the height of fall. The magnitude of the electric current corresponding to the pressure is called *potential*, and its unit is called the *volt*. For the present, however, we do not have to occupy ourselves with this magnitude.

* Apparatus are made which depend on the magnetic action of the current, and on which the strength of the current can be read directly in amperes For chemical purposes an instrument on which milliamperes can be read off, is the most suitable. For the measurement of stronger currents auxiliary apparatus (shunts) are given along with such instruments, which reduce the sensitiveness to a definite fraction, generally a tenth or a hundredth.

190. **The Second Law of Faraday.** —From the law that the ions of the electrolytes are united with definite amounts of electricity, some important conclusions can be drawn, which allow of a considerable extension of the electrochemical relations.

Hydrochloric acid solution is an electrically *neutral* body. If, then, the hydrion in it has a positive charge of the above large amount, there must also be negative electricity of exactly the same amount present. This is united with the chlorine, which thereby passes into chloridion. According to the law of combining weights, there are 35·45 gm chlorine to 1 01 gm. hydrogen ; *consequently, one gram-ion or 35 45 gm. of chloridion, is united with 96,540 coulombs of negative electricity.*

Similarly, the solutions of all salts are electrically neutral. If we consider, for example, such amounts of the different chlorides as contain 35·45 gm. chlorine, the amounts of the metals present along with it must also be united with 96,540 coulombs of positive electricity, independent of their nature. These amounts are equal to the combining weights of the respective metals, which are each united with one combining weight of chlorine ; consequently we can state the universal conclusion : —

The amounts of the different ions united with the same quantities of electricity, are in the proportion of the combining weights of these ions.

In this form, the theorem holds, certainly, only when the combining weights are so chosen that they correspond to 1·01 gm hydrogen or to 35 45 gm. chlorine. There are, however, metals which combine with two, three, or more combining weights of chlorine ; in their case the amount of electricity is a corresponding multiple, and they are called *polyvalent* ; likewise, there are *polyvalent anions* We shall discuss these relations at a later stage.

The theorem just enunciated was also discovered by Faraday, and is also called the law of Faraday. This law, therefore, contains two laws which, indeed, are connected with one another but have respect to different things. Recapitulating all that has been said, we may express it in the following form :—

In electrolytes, the electricity moves only with the simultaneous movement of their components, the ions. The quantity of electricity transported is proportional to the quantities of the ions and amounts to 96,540 coulombs, or a multiple of this, for every gram-ion of any substance.

* The law of Faraday has a certain similarity to that of Gay

Lussac with respect to the volumes of gases in chemical combination. Just as the amounts of gases present in equal volumes are proportional to the combining weights or to multiples of these, the amounts of the ions united with equal quantities of electricity are also proportional to the combining weights or to fractions of these.

* 191. Primary and Secondary Products of Electrolysis.— If very dilute hydrochloric acid is subjected to electrolysis, hydrogen is obtained, as before, at the cathode ; no chlorine, however, appears at the anode, but, in its stead, an equivalent amount of oxygen is evolved.

This is due to the fact that the water is decomposed by chlorine with formation of hydrogen chloride and oxygen, according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$ (p. 172). This process, it is true, takes place with measurable velocity, only in light ; we may, however, assume here, as in similar cases, that the process takes place without light, only very slowly. It can, in fact, be accelerated by platinum and similar catalysers, even in the dark, to such an extent as to become measurable. The occurrence of oxygen in the electrolysis of dilute hydrochloric acid is, therefore, generally interpreted in such a way that it is assumed that chlorine is first formed, and that this then acts on the water, undergoing double decomposition with this to form oxygen and hydrochloric acid ; the oxygen is accordingly called a *secondary* product of electrolysis.

Doubt, however, arises as to this view, because of the fact that it assumes hydrochloric acid to be *decomposed* by the current and to be *formed* again under the same conditions with the co-operation of the water present. Such an assumption can be avoided by means of suitable considerations ; these, however, we shall not put forward here, but we shall formally retain the view just given, which has, in the first instance, no disadvantage and simplifies the discussion.

Such secondary products are often formed when the ions, after they are discharged, do not constitute substances which are stable under the existing circumstances.

Thus, copper and silver, as has been mentioned, are eliminated as metals from their salts ; they are, therefore, *primary* products. If, however, sodium chloride is electrolysed, there is obtained (when concentrated solutions are used), on the one side, chlorine, but at the cathode there is obtained not sodium but *hydrogen*. This arises from the fact that sodium, which would be eliminated as " primary " product, cannot exist in contact with the aqueous solution, but must immediately pass into caustic soda with evolution of hydrogen (p. 84). One may, therefore, again assume that sodium is indeed eliminated, but that at the moment of its passing from the ionic into the metallic state it reacts with the water with formation of the secondary products. As a matter of fact, caustic soda is found at the cathode, for on adding red litmus solution to the liquid, it immediately becomes blue.

If a solution of caustic soda or sodium hydroxide be subjected to

…, hydrogen, for the reasons just given, makes its appearance
…ode. At the anode hydroxidion, OH, is discharged. This
…exist alone, but the doubled compound, O_2H_2, or hydrogen
…is known. This substance, however, on account of its
…, is also not produced, or at least is so only in traces; on the
…the reaction $4OH = 2H_2O + O_2$, occurs, and free oxygen is
…This oxygen, therefore, is also to be regarded as a secondary

…y's law is necessarily fulfilled whether the products of the
…s are primary or secondary. For in the second case, the
…of the secondary substances
…connected with those of the
…by simple chemical equations.
…former must, therefore, neces-
…produced in amounts which
…tional and chemically equiva-
…primary.

…ght changes in the conditions
…periment, one may sometimes
…primary or the secondary
…at will. For example, if, in
…lysis of sodium hydroxide or
…loride, the platinum cathode
…d by one of mercury (Fig. 74),
…gen is evolved but the
…issolves in the mercury. If,
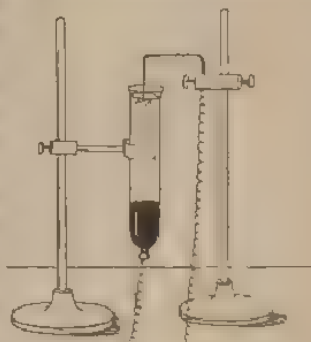
…, the mercury containing the sodium be placed in pure water,
…formation $2Na + 2H_2O = 2NaOH + H$, slowly takes place,
…is evolved and the liquid reacts alkaline.

Dissociation of Electrolytes. An important fact, which
…rther light on the difference between electrolytes and non-
…, is the following. It has previously been explained that
…weight of substances soluble in water, can be determined by
…which they produce in the freezing point of water, one
…substance dissolved in a litre of water causing a depression
…If the quantity of hydrochloric acid which causes such a
…be determined, it is found that about 19 gm. are sufficient.
…smallest molar weight which can be assumed for hydrogen
…is 46, the sum of the combining weights of chlorine and
…this molar weight, also, is obtained from the gaseous density
…chloride (p. 178). New relations, therefore, are met with
…require a special interpretation.

…obtained when we take into account the facts which have
…set forth concerning the *independent behaviour of the ions*.
…se of the other hydrogen compounds, as, for example,
…spirit of wine, water, sugar, etc., no common property can

Further, we shall sometimes find it necessary to distinguish the substances in the condition of ions from the others. For this purpose, the cations will be designated by a point, the anions by a dash. $H^{.}$ represents, therefore, hydrion, Cl', chloridion. *On account of the necessity that chemically equivalent amounts of cations and anions must be present in solutions (p. 197), every complete chemical equation must, when ions occur, in it, contain equivalent amounts of cations and anions on the same side of the sign of equality.*

Thus, for example, the process of the formation of sodium chloride from hydrochloric acid and caustic soda will have to be represented by the following equation, if it is desired to represent the processes by the ions : —

$$H^{.}Cl' + Na^{.}OH' = Na^{.}Cl' + H_2O.$$
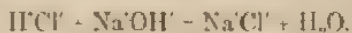
This equation shows that the ions chloridion and sodion remain unchanged in the process, as their reactions, indeed, also persist in the solution of common salt produced. For this gives, on the one hand, the precipitate with silver salts which is characteristic of chloridion, and on the other hand, when electrolysed with a mercury cathode, it yields a solution of sodium in mercury, just as caustic soda also does (p. 199).

The ions hydroxidion and hydrion, however, are used up, because they have combined to form undissociated water (p. 194). For this reason the reaction both of hydrion and of hydroxidion have disappeared, for the liquid no longer reacts acid, nor can the basic properties of caustic soda be any longer detected.

194. Thermochemical Relations of Hydrogen Chloride — Since chlorine burns in hydrogen, the heat developed in the combustion can be directly measured ; the following equation is thus obtained —

$$Cl_2 + H_2 = 2HCl + 2 \cdot 92 \, k_j.$$

This number applies to the formation of *gaseous* hydrogen chloride. If this is dissolved in water, a further very considerable quantity of heat is developed. The necessity is here felt of distinguishing the dissolved hydrogen chloride from the gaseous, since these two forms possess, in conformity with the difference of their properties, very different energy.

Where we are dealing with aqueous solutions, it has become customary to designate the condition of *solution* of substances by the addition of aq (aqua). Now, certainly, the development of heat on dissolving hydrogen chloride varies, according as the solution produced is more or less concentrated. This is easily seen from the fact that on diluting a concentrated solution of hydrochloric acid, a fairly large quantity of heat is developed. If, however, the dilution is carried further, this heat becomes less and less, and there is ultimately a final condition reached when a measurable quantity of heat is no longer developed. It is to this condition that the symbol aq. refers

If hydrogen chloride is dissolved in a large quantity of water, 72 kj are developed, and we have the equation

$$HCl + aq. \quad HCl\,aq + 72\;kj$$
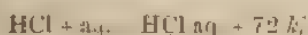
On adding this equation (multiplied by 2) to the preceding one, there follows

$$H_2 + Cl_2 + aq. \quad 2HCl\,aq. + 2 \cdot 164\;kj,$$
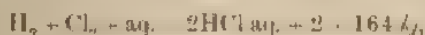
which gives the heat of formation of the *dissolved* hydrochloric acid from its elements.

195. **Thermochemistry of the Salts.**—If a strong acid, *e.g.* hydrochloric acid, is neutralised with a strong base, *e.g.* caustic soda, a quantity of heat equal to 57 kj is developed. The quantity of heat is found to be identical, no matter what acid or base is used, it being assumed that both are "strong," and that both are in the condition of dilute aqueous solution.

The reason of this law becomes at once apparent if we recall the fact that the formation of a salt from its acid and base in dilute aqueous solution, consists in the hydrion and the hydroxidion combining to form water, while the two other ions remain unchanged side by side (p. 202). The heat development of 57 kj is nothing else than *the heat of formation of water from hydrion and hydroxidion.* Since in the formation of any and all salts from strong (*i.e.* nearly completely dissociated) acids and bases, the same process of the formation of water always takes place, the corresponding heat development must also have the same value.

At the same time it follows that deviations are, in general, to be expected, if any of the suppositions made are not fulfilled, *i.e.* if acid, base, or salt is slightly dissociated. To the heat of formation of water, 57 kj, there must then be added the quantity of heat which is developed or absorbed in the decomposition of the acid or base into its ions or in the formation of the undissociated portion of the salt, and the observed heat of neutralisation is the sum of the corresponding magnitudes. We shall have an opportunity later of mentioning such cases.

Further, it was mentioned on p. 193 that the elementary ions have different quantities of energy from the free elements. It may be asked if it is possible to measure this difference.

A method, which cannot be described here, has, indeed, been found for this purpose; but since no other method of attaining the same object could be found, it has hitherto not been possible to test its result. It led to the conclusion that the transformation of hydrogen gas into dissolved hydrion causes no appreciable change of energy. We have, therefore, the following thermochemical equation :—

$$H_2 + aq. \quad 2H^{\cdot}\,aq. + 0\;kj$$
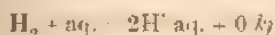
If this basis be assumed, the heats of formation of all other
can be determined.

For example, it was found (p. 203) that a dilute aqueous solu
of hydrochloric acid is produced from its elements and water
a heat development equal to 164 kj. Since this solution cont
chlorine and hydrogen in the form of ions, we should, taking this
account, write the equation : —

$$Cl_2 + H_2 + aq. = 2Cl'H^. aq + 2 \cdot 164 \; kj$$
$$2Cl' \, aq. + 2H^. \, aq. + 2 \cdot 164 \; kj.$$
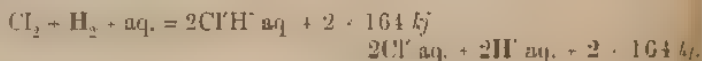
Subtracting from this the equation $H_2 + aq. = 2H^. \, aq,$ th
follows

$$Cl_2 + aq. \quad 2Cl' \, aq. + 2 \times 164 \; kj.$$
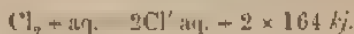
In other words, the heat of formation of dilute hydrochloric acid
equal to the heat of formation of chloridion, since the heat of format
of hydrion is nought.

This conclusion can be at once generalised. Since, as regards
hydrion, the same relations are found in the case of all acids so far
they are electrolytically dissociated, the rule obtains for all acids th
the heat of formation of their dilute aqueous solutions is equal to t
heat of formation of their anion.

When sodium is dissolved in hydrochloric acid, the hydrogen
the acid escapes and sodium chloride is produced The developm
of heat which thereby occurs is very considerable. This has b
determined, indirectly, and been found equal to 239 kj. This cor
sponds, therefore, to the equation

$$2Na + 2H^.Cl' \, aq. \quad H_2 + 2Na^.Cl' \, aq. + 2 \cdot 239 \; kj.$$
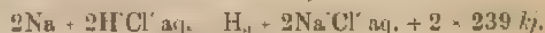
If we again subtract the equation $H_2 + aq. - 2H^. \, aq$ from this and ou
on each side, the common member $2Cl' \, aq.$, we obtain

$$Na + aq. \quad Na^. \, aq. + 239 \; kj.$$
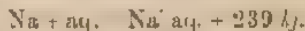
That is to say, the conversion of metallic sodium into sodium
accompanied by a development of heat of 239 kj. This is the s
amount of heat as was developed in the action of sodium on hyd
chloric acid, for the simultaneous conversion of hydrion into gase
hydrogen gives no heat effect.

This theorem, also, can be extended generally. It holds for ev
other dissociated acid and every other metal. We can, therefo
enunciate the general law : —

If a metal acts on an acid with the formation of a salt and general
of hydrogen, the amount of heat which is developed depends only on
nature of the metal, and is independent of the acid. This heat is equal
the heat of transformation of the metal into its cation.

The first part of this law is an experimental fact, and was known ~~ng~~ before it was deduced on the basis of the theory of electrolytic ~~ssociation.~~

Should any of the substances with which we are dealing be undis~~sociated~~ or only slightly dissociated, deviations from the simple law ~~occur~~; the cause of these is the same as in the case of the deviations ~~in~~ the constant heat of neutralisation, discussed on p. 203.

The transformation, therefore, both of chlorine and of sodium, from ~~the~~ ordinary to the ionic condition, is accompanied by a very consider~~able~~ development of heat. Although the difference of the total energy ~~of~~ the two conditions, of which the heat development is an expression, ~~is not~~ a direct measure of the tendency of the elements to pass into ~~the~~ ionic condition, still the one moves to some extent parallel to the ~~other~~, and from the large values of the heat development we can infer ~~a large~~ value for the tendency to transformation. In fact, it has been ~~repeatedly~~ mentioned that both elements possess a very considerable ~~chemical~~ reactivity. On examining the nature of these reactions of ~~chlorine~~ and sodium more closely, it is found that in the majority of ~~the cases~~ *salts* are formed, that is to say, we have before us a mani~~festation~~ of the tendency of chlorine and sodium to exchange the ~~ordinary~~ for the ionic condition.[1]

[1] Even in the *solid* salts, which are not electrolytically dissociated, the components ~~are much~~ nearer to the condition of the ions than to that of the free elements. This is ~~seen from~~ the fact that the passage of the solid salts into the ionic condition, on being ~~dissolved~~ in water, gives rise, in general, to only inconsiderable heat effects, in most ~~cases, indeed,~~ to absorption of heat.

CHAPTER X

196. Oxygen Compounds of Chlorine. — Whereas hydrogen can combine with chlorine only in one proportion, this latter element forms several compounds with oxygen. There is a still larger number of substances which contain hydrogen along with chlorine and oxygen.

All these compounds are distinguished from hydrogen chloride by a circumstance of essential importance. They bear the same relation to it as hydrogen peroxide does to water; hydrogen chloride is formed from its elements with loss of energy, and cannot, therefore, decompose spontaneously into them, but, for the production of the oxygen compounds of chlorine, energy must be communicated. Accordingly these compounds exhibit the property of decomposing spontaneously, i.e. without the communication of energy, and this instability is so marked in the case of some of them that they decompose with explosion. The reason for this is in entire accordance with the relations set forth in the case of hydrogen peroxide (p. 162).

The way in which the energy necessary for the formation of such compounds must be communicated, may vary in different cases. The most frequent and, for general reasons, the most important way for us is the *chemical*. If the possible processes are conducted in such a way that along with the desired substance, other substances are produced whose formation is accompanied by the liberation of large quantities of energy, this energy can be used for the purpose of producing the comparatively unstable compound. For the successful communication of this energy, however, it is not sufficient that any reaction whatever which will yield energy, be allowed to take place along with the desired one; such a reaction would act merely as a corresponding elevation of the temperature, and it would have no effect, or only a harmful one. *On the contrary, it is an essential condition that the two reactions be dependent on one another, or be "coupled" with one another, so that the one cannot take place without the other.* It can be seen from the chemical equation whether this condition is satisfied. If this can be separated into two equations which are independent of one another,

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chemical processes are not "coupled"; if such a separation cannot be made, the above condition is satisfied.

Thus, for example, it might be expected that the large development of energy which accompanies the formation of water from its elements, could cause the simultaneous formation of hydrogen peroxide from oxygen and hydrogen, the energy necessary for this latter reaction being yielded by the former by some such reaction as is expressed by the equation

$$3H_2 + 2O_2 = 2H_2O + H_2O_2.$$
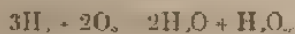
This expectation is not confirmed by experience, a fact which is in harmony with the rule just given, for the equation can be resolved into the two equations

$$2H_2 + O_2 = 2H_2O \text{ and } H_2 + O_2 = H_2O_2.$$

The two processes are, therefore, not coupled or mutually conditioned. Numerous examples of coupled processes will be given by the cases which lead to the formation of the oxygen compounds of chlorine, and which will be given immediately.

Hypochlorous Acid.—It has been already mentioned (p.) that chlorine is absorbed by caustic soda solution. The product formed cannot consist entirely of sodium chloride, for this is formed from caustic soda and *hydrogen chloride*. As a matter of fact, sodium chloride is indeed formed, accompanied, however, by a new substance.

The solution produced has not the purely saline taste of common salt, but a caustic one. Like free chlorine, it has a *bleaching* action on vegetable colours, e.g. litmus; it acts as a powerful disinfectant, and on the addition of hydrochloric acid, it evolves chlorine, which can be detected by its colour and smell. Common salt, however, gives no such reaction with hydrochloric acid.

The above process takes place, according to the equation

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$
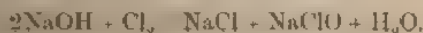
There are formed, therefore, sodium chloride and another compound which contains oxygen.

If this compound, NaClO, be prepared free from sodium chloride, we find that its aqueous solution is an electrolyte, but does not give any ions of chloridion, for no precipitate is obtained with silver nitrate. The crude solution, which contains sodium chloride, of course gives a precipitate, but only in half the amount that corresponds to the chlorine present.

From this it follows that this second substance is, indeed, a salt, but has no chloridion. The chlorine must, therefore, be present in another combination, and the most obvious possibility, and the one which agrees with actual fact, is that it forms an ion ClO' with the oxygen, sodion being the other ion of the salt.

There must therefore be an acid HClO, formed by the combination of hydrogen with the ion ClO′, which on neutralisation with caustic soda again yields the original salt, according to the equation HClO + NaOH NaClO + H₂O.   Such an acid can, indeed, be prepared. This acid has received the name of *hypochlorous acid*, its salts are called *hypochlorites* and the ion ClO′ *hypochloroxion*.   The sodium salt already mentioned is called *sodium hypochlorite*.

198. **Preparation of Acids from their Salts.**—For this purpose a general method is used, which can be described in the following words: *To obtain the acid corresponding to a given salt, the salt is decomposed with another acid.*

That such a preparation is possible can be seen if we designate the desired acid by HA, where A is a simple or complex anion, and its salt by MA, where M represents some metal ion.   Further, if HB is another acid, the following reaction is possible by the interaction of the two substances :

$$MA + HB \quad HA + MB.$$
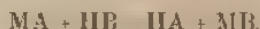
There would be obtained, therefore, if the reaction took place, the desired acid and the salt of the acid added.   There remains then the further task of separating the two substances in order to obtain the acid in a pure state.

Applying this rule at once to the case before us, we should have to decompose the sodium salt NaClO with hydrochloric acid.   The desired acid, along with sodium chloride, would be obtained, according to the reaction

$$NaClO + HCl \quad NaCl + HClO,$$
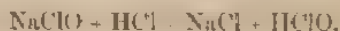
and the two substances would then have to be separated.

It has been found, now, by experience that the reaction represented by the general scheme always occurs, but is *never a complete* one.   In all cases only a portion of the substances present undergoes reaction, and another portion remains unchanged.   In other words, in all these cases chemical *equilibria* are established (p. 101).   For such equilibria it is necessary that the concentrations of the reacting substances shall be in a definite relation to one another, depending on the nature of the substances, on the temperature, and on several other circumstances.

If, now, one of the participating substances is removed, the equilibrium can no longer exist, but the reaction must take place by means of which the substance removed is again replaced.   If the portion thus formed is also withdrawn, the same process goes on again, and in this way the reaction can be carried so far that the total possible amount of the product is ultimately formed.

On this fact is based the preparation of hypochlorous acid by the reaction described.   If dilute hydrochloric acid is added to the sodium

orite, part of the salt is converted into sodium chloride and
orous acid, while another part remains undecomposed.   On
g the mixture, the hypochlorous acid, which is the most vola-
the four substances present, passes over, and the amount of it in
due is diminished.   For this reason fresh acid must be formed
esidue : if this is also removed by distillation, all the acid which
formed from the quantities of the substances present, must
e ultimately formed, and be found in the distillate.   And this
matter of fact, the case.

arrying out the experiment it is necessary to proceed with care
add less hydrochloric acid than corresponds to the equation.
necessary to employ dilute acid, and to so add it that there
here exist an excess of hydrochloric acid.   In the present
is necessary because of the fact that hydrochloric acid
the hypochlorous acid, as will be presently discussed.   In
es, where such action is not to be feared, these precautions
cessary.

Properties of Hypochlorous Acid.—The aqueous solution
hlorous acid, obtained in this manner, shows not only the
properties of acids but also some special properties, which in
es mask the former.   The solution is colourless but has a
ell, similar to that of chlorine.   It acts as a powerful bleaching
wards organic colouring matter, and its action as a disinfectant
poison for small organisms, is almost equal to that of chlorine.
great similarity shown by the solution of hypochlorous acid to
 ation of chlorine, is due to the fact that the latter under
rtial transformation into hypochlorous acid and hydrochloric
ording to the equation

$$Cl_2 + H_2O = HOCl + HCl.$$

reaction, also, does not take place completely, but only
and to an extent which is dependent on the concentration
emperature.   In the reverse manner, hydrochloric acid and
rous acid act on one another with formation of chlorine and
This reaction, however, is also not a complete one, and, there-
rule which has just been given, that the reaction can be made
ace completely in the one or the other direction, by removing
ponding reaction products, will hold also for it.

Decompositions of the Hypochlorites.—The most im
of the special properties of hypochlorous acid depend on the fact
oses its oxygen with extreme readiness, thereby passing into

reason why the decomposition of sodium hypochlorite with hydrochloric
carefully so as to avoid having at any time an excess of the acid
If this care is not observed chlorine is formed, which on distilla-
es with the hypochlorous acid and renders it impure.

P

necessary energy is drawn, almost without exception, from the heat contained in it. To this class belong, therefore, all processes which take place spontaneously with fall of temperature. Examples of this are not rare. A volatile liquid evaporates spontaneously with fall of temperature into a space which is free from its vapours; salts dissolve spontaneously in water with fall of temperature, and many chemical processes also take place spontaneously with fall of temperature. All these cases are examples of the fact that in spite of the decrease of the free energy in processes which take place spontaneously, the total energy can increase.

The question as to how the free energy is to be measured cannot be discussed here. It is sufficient to know that the fact that a reaction takes place spontaneously is a sign that the free energy of the system is thereby diminished.

If we apply what has here been said to the case we were just considering, the system chlorine plus caustic soda will be designated as the form with the *greatest* free energy. The system produced from this, sodium chloride plus sodium hypochlorite, has *less* free energy, and sodium chloride plus oxygen has the smallest amount of free energy. The following figure gives a picture of the relations, the values of the free energy being represented by the perpendicular heights :—
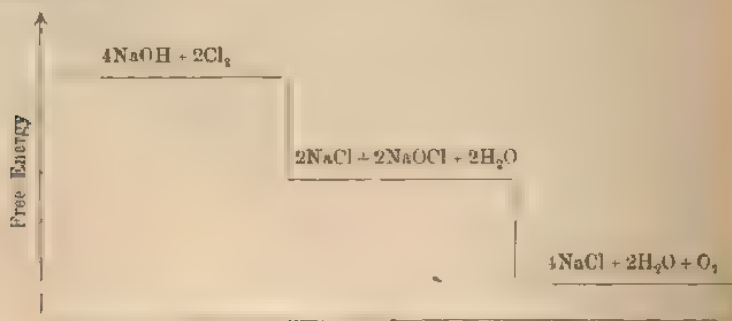
From the appearance of the figure it will be seen why it is that, starting from the highest step, the lowest is not immediately reached, but that a halt is first made at the middle one. This furnishes an answer to the question asked above (p. 210).

203. Chlorine Monoxide. Hypochlorous acid is not known in the pure, *i.e.* the anhydrous, state. On attempting to prepare it, the elements of water leave the acid, and a compound of chlorine and oxygen remains behind. This compound is no longer an acid, since it contains no hydrogen.

This process takes place in accordance with the equation

$$2HClO \quad H_2O + Cl_2O.$$

The new substance is called chlorine monoxide, since it contains *one* combining weight of oxygen. Since it is obtained from hypochlorous acid by loss of water, it is also called *hypochlorous anhydride*. This nomenclature is employed fairly generally ; various substances which are formed from other substances by the loss of the elements of water, are called *anhydrides* of these substances.

* This name was introduced on the supposition that in the original substances not merely the elements of water are contained but also "ready formed" water, and this conjecture arose because some substances gave off water with exceeding readiness and rapidity. But a deeper knowledge of the facts has shown that there exists a continuous transition from those which readily give off water to those from which water can be obtained only by especially powerful reactions. It is, therefore, more scientific to in no case assume the presence of pre-formed water, especially as no definite meaning can be attached to such a supposition.

Chlorine monoxide is obtained most readily by carrying out the reaction leading to the formation of a salt of hypochlorous acid (p. 209), with an oxide from which the salt is not formed. For this purpose *oxide of mercury* is the best. When a current of dry chlorine is passed over mercuric oxide,[1] the following reaction takes place :—

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$
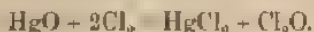
In this equation Hg is the symbol for mercury ; its oxide is composed of equal combining weights of mercury and oxygen. The chlorine compound of mercury, or mercuric chloride, remains behind as a solid substance, and the *chlorine monoxide*, which is gaseous at room temperature, escapes and can be collected.

Chlorine monoxide is a yellow-brown gas with a strong, unpleasant smell, which can be condensed to a liquid at 5°. It dissolves in water, passing slowly into hypochlorous acid. In the gaseous and still more in the liquid state, it is very unstable and readily decomposes with explosion, forming oxygen and chlorine. These explosive properties find an explanation in the fact that heat is liberated by the decomposition (p. 162). The gas also decomposes into its elements under the influence of light, but generally without explosion.

204. Chlorates.—The steps in the transformation of chlorine and caustic soda described on p. 212 are not the only possible ones, for there are still two others which lie between the middle and the lowest. The solution of NaCl + NaOCl, which is obtained by passing

[1] In order that the reaction may take place satisfactorily, the mercuric oxide required for this experiment must be of a special nature. If too finely divided, the reaction goes too quickly and an explosion may occur ; if it is too coarse, the reaction will be too slow and the gas will be contaminated with chlorine. A suitable oxide is obtained by gently heating the oxide prepared by precipitating mercuric chloride with caustic soda in aqueous solution.

chlorine into a solution of caustic soda, undergoes a change in its properties on being kept some time. This change takes place more quickly in the heat and when a slight excess of chlorine is present in the solution. Its bleaching power and its smell gradually disappear, and after some time it contains no more hypochlorite, for it evolves no chlorine on being treated with dilute hydrochloric acid in the cold.

If the solution is now evaporated, two salts are obtained—sodium chloride and another salt which, like sodium hypochlorite, also contains oxygen. It is shown, however, by analysis, to have a composition which is expressed by the formula $NaClO_3$, and is called *sodium chlorate*. It is, therefore, the sodium salt of a new anion, *chlorion*, ClO'_3. This ion is also not precipitated by silver salts; almost all the salts which it forms are readily soluble. The reactions which take place are, therefore, represented by the equations

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O,$$
$$3NaOCl = 2NaCl + NaClO_3,$$
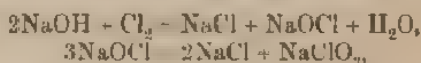
or, omitting the intermediate stage,

$$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O.$$
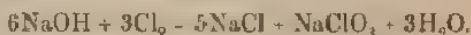
Since sodium chlorate is a very soluble salt, and can be separated only with difficulty from the simultaneously formed sodium chloride, it is better to prepare the corresponding *potassium salt* by passing chlorine into a solution of potassium hydroxide. Since potassium in all its chemical relations exhibits an exceedingly great similarity to sodium, the reactions which take place are of exactly the same kind as those described, and need not be again explained. *Potassium chlorate*, along with potassium chloride, is obtained as the product of the reaction; and since the former salt is much less soluble than the latter in the cold, it separates out on allowing the solution, obtained by the action of chlorine on potassium hydroxide, to cool.

The salt thus obtained is already well known; it is the salt used for the preparation of oxygen in the laboratory (p. 63). The potassium chloride formed at the same time is a salt very similar to sodium chloride.

From what was previously stated, it is known that potassium chlorate, on being heated, decomposes into oxygen and potassium chloride, the same behaviour being likewise shown by sodium chlorate. The decomposition takes place according to the equation

$$2KClO_3 = 2KCl + 3O_2,$$
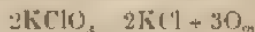
where K is the symbol for potassium.

As can be seen, this is the last step in the action of chlorine on hydroxides, and to the three steps given on p. 212 there must be added a fourth, between the hypochlorite and the lowest. We shall soon see that even a fifth step must be inserted.

In conformity with the smaller fall between the chlorate and the given steps, the last transformation does not proceed so readily and fully as that of chlorine into hypochlorite, and of the latter into chlorate. At ordinary temperatures, the chlorates are practically quite stable, and only at comparatively high temperatures does the reaction become so rapid that it can be observed. That the reaction can be accelerated through the influence of catalytic agents, has already been mentioned (p. 63), besides the substance then mentioned, pyrolusite, oxide of iron is a very effective accelerator of the decomposition.

205. Preparation of Chloric Acid. Chloric acid cannot be easily obtained from potassium or sodium chlorate. The aqueous solution of the salt, it is true, undergoes partial decomposition by other acids, in accordance with the general rule (p. 208); but as the free acid cannot be distilled, the separation cannot be carried out in the same way as in the case of hypochlorous acid. Recourse has, therefore, to be had to another method.

If we consider the equation

$$MA + HB = MB + HA$$

given on p. 208, we see that the desired acid can be prepared not only by removing it from the sphere of the reaction, but also by completely removing the salt MB. As a rule, certainly, the salts are non-volatile, so that the method of distillation used for removing the acids cannot be employed. On the other hand, however, many salts are insoluble, and by their precipitation the reaction is made as complete as by the removal of the acids.

To carry this idea into practice, the ions M and B have only to be chosen so that they together give an insoluble salt; that is to say, a salt of the desired acid has to be prepared which yields an insoluble salt with another acid, and with this acid the salt has to be decomposed.

Now, we already know a metal which gives an insoluble salt with hydrochloric acid, viz. silver. Silver chloride is so very sparingly soluble that even very dilute solutions of chlorides and silver salts give a precipitate (p. 191). In the general equation, therefore, M can be replaced by silver and B by chlorine. If silver chlorate be prepared and be decomposed with hydrochloric acid, silver chloride and chloric acid are formed according to the equation

$$AgClO_3 + HCl = HClO_3 + AgCl,$$
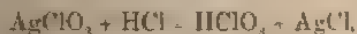
where Ag is the symbol for silver.

Silver chlorate can be obtained in the same way as sodium or potassium chlorate, by the action of chlorine on silver hydroxide.

The same principle can be carried out in various other ways, since every insoluble salt gives a possible combination. Indeed, for the

actual preparation of chloric acid, other substances are mostly employed, especially *barium chlorate* and *sulphuric acid*. With these the same result is obtained, since barium sulphate is also a very difficultly soluble salt.

In employing this method of preparation, the amounts of the reacting substances must be determined exactly, so that neither the one nor the other shall be in excess and contaminate the chloric acid which remains behind. In the method itself, however, is contained a security against this, for the one substance must be added to the solution of the other only so long as a precipitate is formed. The clear liquid is tested with a small quantity of the first substance to see if an excess of the second has not been added, and one continues testing with the two substances alternately until a sample of the solution gives no precipitate either with the one or with the other.

* It must not be thought that in this way an "absolutely" pure solution is obtained. This would be the case only if the precipitate were absolutely insoluble, which, however, is never the case. When, however, the solubility of the precipitate is known from other measurements, the amount of impurity still present can be calculated.

The solution of chloric acid thus obtained, is a strongly acid, colourless liquid, which, although fairly stable in dilute solution, slowly decomposes into oxygen and hydrochloric acid. The latter substance acts in turn on the remaining chloric acid with formation of chlorine and water, so that oxygen and chlorine are finally obtained. Expressed in equations, we have

$$2HClO_3 = 2HCl + 3O_2,$$
and
$$5HCl + HClO_3 = 3H_2O + 3Cl_2,$$
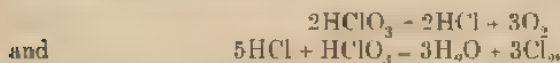
or, combined together,

$$4HClO_3 = 2H_2O + 2Cl_2 + 5O_2.$$
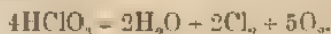
The decomposition takes place all the more rapidly the more concentrated the solution becomes and the higher the temperature rises. By reason of the large quantities of oxygen which are evolved in the decomposition, chloric acid is a strong oxidising agent.

Chloric acid as such finds no application, but the chlorates are largely used. Fuller information with regard to this will be given under the respective metals.

206. **Solubility of Salts.**—In order to successfully perform the above-mentioned separation of two salts by crystallisation, on the basis of difference of solubility, a knowledge of the general laws to which the solutions of solid substances are subject, is necessary. The most important of these are the following.

When a solid substance dissolves in a liquid, there is for each temperature a definite *solubility, i.e.* a definite ratio between the amounts of the dissolved substance and of the solvent. This ratio

... be expressed in two ways: either by taking the total amount of ... solution or only the amount of the solvent, as unit, or putting it ... al to 100. The former method of calculation is the one most ... able for scientific purposes, but the latter is almost entirely used, ... we shall retain it here. The *solubility* will, accordingly, be ... resented by the amount of solid substance which can dissolve in ... parts of the solvent.

If less of the solid substance is brought into contact with the liquid ... corresponds to the solubility, it all dissolves and the solution is ... *unsaturated*, because it can still take up further quantities of the ... substance. If more of the solid substance is added, an amount ... corresponding to the solubility, and the excess remains undis-... The solubility is quite independent of the amount of this ... and the same concentration is therefore found, whether the ... is in contact with much or with little of the solid substance.

The solubility is therefore an expression of the equilibrium between ... and the liquid portion, just as, for example, the melting point ... single substance is an expression of the equilibrium between the ... and the liquid form. In both cases, the equilibrium is independ-... of the relative and absolute amounts of the participating phases. ... statement applies quite universally to all equilibria between different ...

When the solid substance is not present, one of the factors of ... equilibrium is wanting, and there is no cause present to prescribe ... definite concentration. From this it follows that a solution *alone* ... not have a definite concentration. In the case of *unsaturated* ... this requires no further explanation; as small quantities of ... substance as we please can be dissolved in a given quantity ... liquid. The theorem, however, must also apply to more concen-... solutions, *i.e.* there can be solutions which contain more of the ... substance than corresponds to the condition of equilibrium in ... of the solid form.

As a matter of fact, such solutions can be prepared in various ... If the solid substance is not present, they are, within certain ... just as stable as the unsaturated solutions; in contact with the ... form, however, they behave in the opposite way to these. ... the unsaturated solutions dissolve the solid form, there ... from the *supersaturated* solutions, as they are called, so ... the solid substance that the condition of saturation is again ...

Influence of Temperature and Pressure on the ... ability. If the temperature changes, the solubility in general ... changes. In the case of most solid substances, the solubility ... as the temperature rises; in the case of some, however, it ... The change of solubility with the temperature is usually ... by a curve, the temperatures being measured towards the

procedure is known as *recrystallisation*. Of the substances given in Fig. 75, potassium chlorate can be recrystallised very well from its solutions, since the difference of solubility at different temperatures is very great. The method is less suitable for potassium chloride, and not at all suitable for sodium chloride. For the purpose of recrystallising these substances other means must be employed by which the solid substance is caused to separate out.

* These differences of behaviour can be made clear by an experiment. If potassium chlorate be added to boiling water as long as it dissolved, so much of the salt is deposited on cooling that the liquid forms a firm paste. From a solution of potassium chloride saturated in the heat, a much smaller amount of crystals is deposited, and from the solution of sodium chloride, practically none.

Solutions may be made to crystallise not only by change of temperature but also by diminishing the amount of solvent. In the case of volatile liquids this is best effected by *evaporation*. Thus, for example, by evaporating the water of the naturally occurring solutions of common salt, the *salt springs*, the salt contained in them is obtained in the crystalline condition. This method of *crystallisation by evaporation* is used almost more frequently than the method of crystallisation by cooling.

210. Behaviour of Mixed Salts.—Regularities similar to those just set forth obtain in the case where several salts, or, generally, several solid substances, are present at the same time. In this case also there corresponds to each temperature a definite condition of saturation which is independent of the relation between the amounts of the different phases. When several salts are present the solubility of each single salt, certainly, is no longer the same as when it is present alone, but they exercise a mutual influence on one another. This, however, affects only the numerical values and not the general relations.

If, now, the point of saturation of a mixed solution is exceeded, this does not, in general, occur at the same time for both salts, but the solution which is supersaturated for the one is still unsaturated with respect to the other. For this reason only the *one* solid substance separates out from the solution, and its separation from the other is thus effected.

For example, on evaporating a solution of any mixture of salts only that salt will, in the first instance, separate out whose point of saturation is first reached. On withdrawing the crystals which are deposited from the solution, the substance is obtained in the pure state. Only when the point of saturation of the other substances is reached do these separate out along with the first, and mixtures are obtained.

In such cases the separation can generally be carried further by making use of the different variation of the solubilities with the temperature. For example, if a solution of potassium chloride and

is to say, when hypochlorous acid decomposes into hydrochloric acid and oxygen, 39 kj are developed. When, therefore, hypochlorous acid acts as an oxidising agent, the heat which is thereby developed for each combining weight of oxygen, greater by 39 kj than if oxidation took place with free oxygen. This would suggest that hypochlorous acid, quite apart from its greater velocity of reaction, must be a stronger oxidising agent than free oxygen, and that it will be capable of oxidising substances not oxidised by this.

This makes us return to the point mentioned on p. 210. Since the decomposition of hypochlorous acid into oxygen and hydrochloric acid takes place with considerable diminution of the free energy, it can be used for the purpose of preparing oxides which could be formed from oxygen only with increase of the free energy, and which, therefore, cannot directly formed from it. Since the taking up of oxygen from hypochlorous acid by the substances in question necessarily takes place simultaneously with the decomposition of the acid, we have here a "coupling" which has been characterised as a presupposed condition of using the free energy of one process to render another process possible (p. 207). Thus, for example, dilute hydrochloric acid can be oxidised to chlorine and water by means of hypochlorous acid in a process which is not possible with free oxygen, because the formation of free oxygen from chlorine and water takes place ...

The heat of formation of *chloric acid* is given by the following equations

$$H_2 + Cl_2 + 3O_2 + aq. = 2HClO_3 aq. + 2 \cdot 100\,kj.$$
$$2Cl_2 + 5O_2 + aq. = 4HClO_3 aq. + 4 \cdot 13\,kj.$$
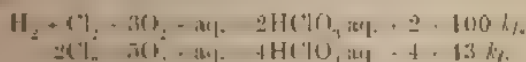
From this we obtain the heat evolved in oxidation by means of chloric acid

$$HClO_3 aq = HCl aq + 3O + 64\,kj$$
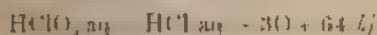
There is a heat evolution, therefore, of 21 kj for each combining weight of oxygen. This number is considerably smaller than in the case of hypochlorous acid, which is in agreement with the smaller oxidising power of chloric acid

For *perchloric acid*, the corresponding equations are :—

$$H_2 + Cl_2 + 4O_2 + aq = 2HClO_4 aq. + 2 \cdot 161\,kj$$
$$2Cl_2 + 7O_2 + aq. = 4HClO_4 aq. + 4 \cdot 18\,kj$$
$$HClO_4 aq = HCl aq + 4O + 3\,kj.$$
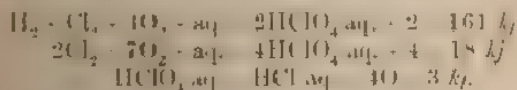
In all three equations the greater stability and feebler oxidising action of perchloric acid finds expression.

215. The Combining Weight of Chlorine.—For the purpose of determining the combining weight of chlorine with sufficient exactness, a somewhat indirect method has been found necessary. First,

Q

potassium chlorate was converted, by heating, into potassium chloride and oxygen. Calculating, in accordance with the equation

$$KClO_3 = KCl + 3O,$$
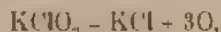
how much potassium chloride is combined with $3 \times 16 = 48$ parts by weight of oxygen, the number obtained represents the combining weight of potassium chloride referred to oxygen equal to 16. Since, now, every gram of potassium chlorate on ignition leaves a residue of 0·6085 gm., losing, therefore, 0·3915 gm. oxygen, we have the proportion

$$KCl : 48 = 0·6085 : 0·3915,$$

which gives for the combining weight of potassium chloride, KCl = 74·59.

Next, it was determined how much silver chloride could be obtained from a given amount of potassium chloride. Since one combining weight of chlorine is contained in each salt, the ratio of the weights in which the one is formed from the other is also equal to the ratio of their combining weights. It was found that from each gram of potassium chloride, 1·9224 gm. silver chloride was obtained. Hence,

$$AgCl : 74·59 = 1·9224 : 1,$$

from which we find, AgCl = 143·39.

Lastly, a weighed quantity of silver was converted into silver chloride. Each gram of silver yielded thereby 1·3284 gm. silver chloride, taking up, therefore, 0·3284 gm. chlorine. Calculating with the aid of this relation how much chlorine is contained in one combining weight of silver chloride, the combining weight of chlorine is found from the proportion

$$Cl : 143·39 = 0·3284 : 1·3284$$

to be, Cl = 35·45.

From these determinations, we can further obtain the combining weights of silver and potassium. Subtracting the combining weight of chlorine from the combining weight of silver chloride which was found equal to 143·39, there follows, Ag = 107·94. A similar calculation in the case of potassium chloride yields K = KCl − Cl = 74·59 − 35·45 = 39·14.

The reason that such an indirect method has been employed is due to the fact that the simple oxygen compounds of chlorine cannot, on account of their unstable nature, be prepared sufficiently pure nor analysed with sufficient exactness. The transformations above described, however, can be performed with very great exactness, and this is the determining reason for preferring the indirect to the direct method.

soda, which was indicated on p. 212, must, in accordance with what has been said, be completed as follows :—
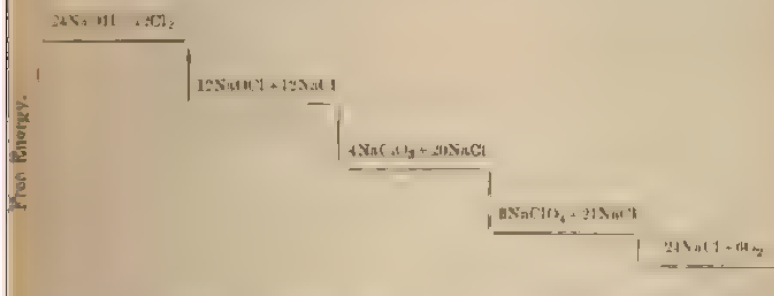
For the sake of shortness, the $12H_2O$, produced in the passage to the second stage, have been omitted, since they take no further part in the transformations.

213. Other Oxygen Compounds of Chlorine.—The substances hitherto described do not exhaust the possible number of compounds of chlorine with hydrogen and oxygen, although the substances still to be treated are of inferior importance to those already mentioned.

If a chlorate is decomposed with a strong acid, e.g. sulphuric acid, chloric acid is first formed, in accordance with the general scheme. This substance is, however, not stable in the anhydrous condition, and immediately undergoes decomposition, in accordance with the equation

$$4HClO_3 = 2H_2O + 4ClO_2 + O_2.$$
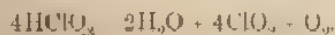
In other words, water is formed from the components of the acid, this being necessary for the production of the (more stable) ion of chloric acid.

The compound ClO_2, formed at the same time, bears the name of *chlorine dioxide* or *chlorine peroxide*, and appears as a yellow-brown gas which can be condensed to a similarly coloured liquid at a temperature under 10°. Both gas and liquid are extremely explosive. This can be shown by placing on the bottom of a wide-mouthed bottle of 2 to 3 litres capacity, a small dish containing some potassium chlorate and allowing a few drops of concentrated sulphuric acid to fall on this. The yellow gas is evolved with a peculiar crackling sound due to small explosions. If a warm metal rod, the temperature of which can be much below that of the visible red heat, be introduced some moments later into the gas, this decomposes with loud detonation into chlorine and oxygen.

Chlorine peroxide is not the anhydride of any definite acid, but, when brought in contact with caustic soda, yields sodium chlorate and

after 5 to 10 minutes.   This appears remarkable, since the differen of density as compared with hydrogen is much greater than th compared with air, and, therefore, the work to be performed agai gravity is also greater.   That, nevertheless, bromine vapour a hydrogen mix more quickly is due to the fact that *diffusion* procee more rapidly in hydrogen because, in this case, the mutual friction the gases is less   The velocity of diffusion obeys, to some exten though by no means exactly, the same law as the velocity of effusi (p. 95), and is, in the case of hydrogen, about four times as gr as in air.

From determinations of the density of bromine vapour, its mo weight has been found to be 160, or five times as great as that oxygen.   Bromine vapour is, therefore, 5 5 times as heavy as a Since the combining weight has been found to be half as great (th exact figure being 79 96), the composition of bromine vapour is rep sented by the formula Br_2.   At very high temperatures, the mo weight becomes somewhat less.   Since similar relations are found an have been more fully investigated in the case of iodine, we shall dis us this phenomenon at that point.

Bromine dissolves in water, forming a yellow to brown colour liquid, which possesses the smell of bromine and can be used in plac of pure bromine when only a small quantity of the substance required.   The solution, saturated at room temperature, contain about 3 per cent of bromine.   If the water contains saline com pounds of bromine in solution, more bromine is dissolved, readil decomposable compounds of bromine being formed which, in mo of their relations, behave like free bromine.   These relations, als will be discussed more fully under iodine.

From the aqueous solution of bromine (bromine water) the separates out, on cooling, a solid hydrate which behaves quite similarl to chlorine hydrate (p. 173).

217. Hydrogen Bromide.—With hydrogen, bromine forms compound, HBr, which is very similar to hydrogen chloride.   Th reaction between the elements, however, is not nearly so vigorous in the case of chlorine.   If bromine vapour be mixed with hydrogen no sudden reaction takes place either on passing an electric spark or on exposing the mixture to sunlight ; only a partial combination of th gases occurs   The reaction can be accelerated by employing catalyti agents, and for this purpose, platinum and the metals like it hav been found to be specially active.   If a suitable mixture of hydroge and bromine vapour be passed through a gently heated tube filled wit finely divided platinum, the issuing gases contain large quantities hydrogen bromide, and, by suitable arrangement, the reaction is practi cally complete.

Hydrogen bromide is obtained more easily, and in a mann more suited for experimental purposes, by the simultaneous actio

ine and phosphorus on water. The chemical reaction which
kes place cannot be completely explained till we come to
rus; suffice it to indicate that a partition of the elements of
esults. The oxygen combines with the phosphorus and the
m with the bromine. Bromine alone is not able to decompose
this would be associated with an increase of the free energy
). If this reaction, however, be joined with another in which a
rable diminution of the free energy occurs, so that over the whole
there is a diminution of the free energy, the reaction becomes

The auxiliary process in this case is the combination of
with phosphorus, which, as we know (p. 64), is accompanied
liberation of large quantities of energy.

experiment is carried out as follows. Red phosphorus along
me water is placed in a small flask, through the cork of
ses a dropping funnel containing
e and a delivery tube (Fig. 76).
is connected a U tube filled
istened red phosphorus spread
pieces of glass. The purpose
is to convert any bromine
which may escape from the
so into hydrogen bromide. On
g the bromine to drop slowly
e flask, a violent reaction, ac
ied by flashes of light, takes
nd from the end of the U tube a colourless gas escapes which
ense fumes in the air and is absorbed with extreme readiness
er. It thus behaves very similarly to hydrogen chloride
gas cannot be collected satisfactorily over mercury, since it is
osed by this metal, mercury bromide and hydrogen being
; still the reaction does not proceed rapidly. On account of
density it can be collected, like chlorine, by displacement of
. In this case the appearance of a thick mist at the mouth is
n that the vessel is full.

molar weight of hydrogen bromide is 81, corresponding to
ula HBr. The gas shows noticeable deviations from the
aws.
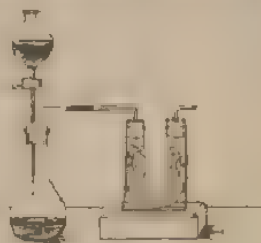
pressure and cold, hydrogen bromide can be converted into a
which boils at 73, and, like liquid hydrogen chloride, has
comparatively slight reactivity.

The Solution of Hydrogen Bromide. An aqueous solu
hydrogen bromide can be obtained by connecting to the
ng apparatus (Fig. 76) the arrangement described on p. 183
absorption of a gas. The solution, saturated at 0, contains 80
of hydrogen bromide; it is very strongly acid, fumes in the
has a density of 1.5. More dilute solutions do not fume so

much, and the 48 per cent solution is in the same condition as the
per cent solution of hydrogen chloride; it distils over with unchang
composition. The relations described in the case of hydrogen chlori
(p. 185) are repeated quite similarly in the case of hydrogen bromid
so that they need not be again described.

The characteristic reactions of acids are displayed in the same w
by hydrogen bromide as by hydrogen chloride, so that equivale
solutions of the two acids behave almost identically, not only qua
tatively but also quantitatively. Hydrobromic acid, therefore, belong
to the strongest acids, and even in moderately dilute solutions
largely dissociated into its ions.

Hydrobromic acid acts on the metals in the same way as hydr
chloric acid: *hydrogen* is evolved and the *bromides* of the metals a
formed. These are identical with the compounds which are obtaine
by the action of the hydroxides of the same metals on hydrobromi
acid, water being simultaneously formed, and with those obtained b
the direct action of bromine on the respective metals.

In the latter case the action is, in general, not so energetic as
the case of chlorine, but the difference is not very great. An in
this is obtained by introducing a piece of thin rolled metallic ti
(tinfoil), such as is used for wrapping up chocolate and such thing
into liquid bromine contained in a test tube. The two element
immediately combine with the production of a dark red flame an
the evolution of thick vapours. On account of the poisonous pr
perties of these, the experiment must be carried out in a fu
chamber with good draught.

The aqueous solutions of hydrobromic acid and of most of th
metallic bromides contain bromine as *bromidion*. In this form
exhibits the general property of ions of electrolytic conductivity, a
the numerical values of this generally agree very closely with tho
of the equivalent chlorides. A reaction with *silver* solutions is a
given, and the precipitate of silver bromide which is produced by sil
salts in all solutions containing bromidion is very similar to silv
chloride in appearance, but is of a yellowish colour and is much le
soluble than silver chloride. The reactions by means of which the tw
substances can be distinguished from one another will be given unde
silver. For the rest, bromidion is not coloured.

When chlorine is passed into solutions containing bromidion a
exchange of conditions takes place: the chlorine passes into chlori
and bromidion into bromine. For this reason, all such solutions o
addition of chlorine water become yellow in colour, and since thi
coloration is quite visible even with a very small concentration o
bromine, it serves as a test for bromidion. Since chloridion cannot,
course, react with chlorine, chlorine water can also be used to di
tinguish between bromidion and chloridion, and for the identificati
of the former in presence of the latter.

Employing a dash to indicate the ions, as mentioned on p. 202, reaction in question would be written,

$$2Br' + Cl_2 = 2Cl' + Br_2.$$
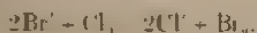
No bromidion, of course, can be present in solution unless an equivalent amount of some cation be also present; the latter, however, takes no part in the process, which takes place in the same way what the cation may be.

This reaction is used for the preparation of bromine from the goods in which bromine compounds occur naturally, more especially the mother liquors obtained in the working up of the potassium salts at Stassfurt (p. 52). All these salt solutions contain the bromine in the ionic form, and on passing in chlorine and distilling the liquid, the readily volatile bromine passes over with the steam. The chlorine used for this purpose can also be prepared in the liquid itself by a hypochlorite (e.g. bleaching powder), for example, and then hydrochloric acid. By means of a preliminary determination of the amount of bromine in the liquors, however, care must be taken rather to add too little than too much chlorine, in order that the bromine evolved be not contaminated with chlorine.

219 Oxy-acids of Bromine.—Bromine is readily dissolved by a solution of caustic soda, the liquid remaining bright yellow in colour. Besides sodium bromide, the liquid then contains *sodium hypobromite*. The reaction agrees entirely with the corresponding one in the case of chlorine, for it takes place according to the equation

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

The solution produced is used in the laboratory. It contains hypobromite, BrO', and by reason of the oxygen of the latter it has as powerful an oxidising action as hypochlorite solution.

Its corresponding acid, hypobromous acid, HOBr, can also be prepared in dilute aqueous solution. It is very similar to hypochlorous acid.

On standing some time, especially when an excess of bromine is present, the solution passes into one containing *bromation*, BrO_3, along with bromidion. In this case also it is better to use a solution of potassium hydroxide. On adding bromine to such a solution without heating until its colour is permanent, the potassium bromate separates at once in the form of a crystalline precipitate. Neglecting the intermediate hypobromite stage, the reaction is

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$$
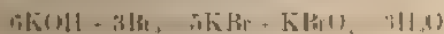
From this salt bromic acid, HBrO_3, can be obtained in aqueous solution in the *same way as chloric acid* was obtained from chlorate

It is very similar to chloric acid, only still more easily decompose[?]
It is not known in the anhydrous condition.

Perbromates have not yet been prepared, and no oxygen compoun[?]
of bromine is known corresponding to chlorine monoxide and chlor[?]
dioxide. In general, the compounds of bromine containing oxyg[?]
decompose more easily than the corresponding chlorine compounds.

The *combining weight of bromine* has been determined in a manne[?]
similar to that used for chlorine. It amounts to 79·96, or almo[?]
exactly 80. The deviation from the round number, however, is n[?]
due to experimental error, but has been proved beyond doubt.

B. *Iodine*

220. General.—Iodine is allied to chlorine and bromine, and form[?]
a third similar element. Of the three, it has the highest combining
weight, amounting to 126·86, and its properties show deviations from
those of bromine chiefly in the same direction as those of bromine
deviate from chlorine.

At ordinary temperatures, iodine is a solid, crystalline substance
of a purple-black colour with an indication of metallic lustre. Its
density is 5. At 114 it melts to a deep brown liquid. Even at
ordinary temperatures it emits some vapour, which can easily be
recognised by its reddish-purple colour when a little iodine is con[?]
tained in a fairly large vessel. Iodine, however, does not bo[?]
till 184 .

Iodine vapour is of a fine violet colour. For the purpose of
observing this colour and at the same time also the great density of
iodine vapour, a large, round-bottomed flask is strongly heated in a
large flame, being kept diligently turned the while, and a few crystals
of iodine are then thrown into the hot flask. The iodine is at once
converted into a vapour of a dark violet colour, which remains at the
bottom, and which, when the vessel is moved, shows itself in a high
degree subject to the force of gravity.

The density of iodine vapour is very considerable, being about
nine times as great as that of air. The molar weight is 254 and the
vapour has, therefore, the formula I_2. An account of its behaviour at
high temperatures will be given presently.

In water, iodine is only sparingly soluble, but still sufficiently for
the brown colour with which it passes into solution to be detected in
fairly thick layers. If a salt-like iodide is present in the water, much
larger quantities are dissolved with a brown colour. This is due to the
formation of an ion I_3, as will be immediately discussed.

In other liquids, iodine is generally more soluble. In spirit of
wine it dissolves with a brown colour similar to that of the aqueous
iodide solutions. This solution is used in medicine, and is calle[?]

... of iodine.   Other solvents, such as carbon disulphide and chloroform, dissolve it with a fine violet colour similar to that of its vapour.   On what these differences of colour depend is as yet known, but it appears that in the brown solutions easily decomposable compounds are formed between iodine and the solvent.

If an aqueous solution of iodine is shaken with carbon disulphide,[1] the colour of the iodine disappears from the aqueous solution, and the carbon disulphide is coloured purple.   The iodine, therefore, leaves the water in order to dissolve in the carbon disulphide.   This is an example of a general phenomenon which is subject to definite laws.

The Law of Distribution.   If to two liquids A and B, which are not (or rather, are only slightly) miscible with one another, a substance be added which is soluble in both, this substance will, in general, dissolve in both liquids and a state of equilibrium will be established. This state is determined by the law that *the substance is distributed between the two solvents in such a way that the ratio of its concentration in the two is constant.*

This ratio is independent of the amounts of the two solvents, and of the absolute concentration, at least within definite limits, and depends only on the nature of the three substances and on the temperature.

For example, iodine is distributed between water and carbon disulphide in the ratio 1 : 600.   If, then, any quantities whatever of water, iodine, and carbon disulphide are shaken together and the two solutions then investigated, there will be found in each cubic centimetre of the carbon disulphide solution 600 times as much iodine as in one of the aqueous solution.

As is evident from these numbers, the concentration in carbon disulphide is very much greater than in water; for this reason, also, the greater part of the iodine passes, as the experiment shows, into the former, when an aqueous solution of iodine is shaken with carbon disulphide.

This law holds only for the iodine present in the elementary state, and not for any compounds of iodine that may be present. If carbon disulphide be rendered a deep violet colour with iodine and the solution then shaken with a solution of caustic soda, the violet colour disappears and the iodine passes into the aqueous solution.   Here, however, it no longer exists as iodine, but has formed salts with the caustic soda.[2]   If hydrochloric acid be added to solution, by which means free iodine is again formed, and the whole be shaken, the carbon disulphide again becomes violet in colour.

---

[1] Carbon disulphide is a compound of sulphur and carbon, and forms a heavy, liquid which does not mix with water.

[2] The reactions which take place here agree entirely with those given by chlorine on caustic soda, and the reader is, therefore, referred to the explanation of these previously (p. 207).

222. Iodine Vapour.—It has already been mentioned that the vapour of iodine has the molar weight 254. This value holds for temperatures above the boiling point up to about 500°. If the temperature be raised still higher, the iodine vapour expands more than a normal gas, and its molar weight, therefore, becomes smaller. The deviation becomes all the greater the higher the temperature is allowed to rise. At 1500°, finally, the half value is reached, and a further elevation of the temperature has no longer any effect.

This statement is true only when the pressure is equal to an atmosphere. If it is less, too small densities are found even at lower temperatures, and the half value is sooner reached. At temperatures above this, however, the molar weight again remains constant. These
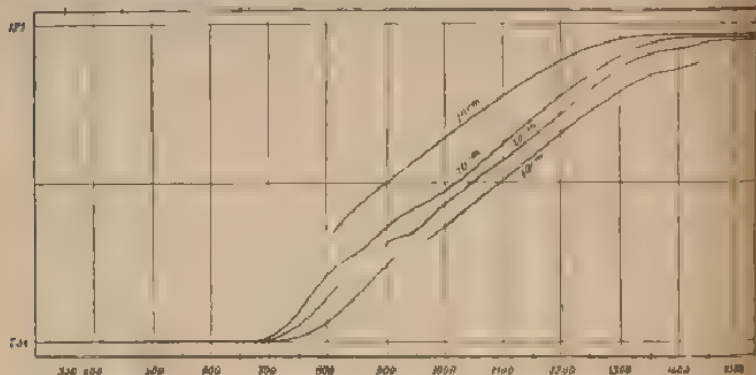
Fig. 77

relations are made clear in Fig. 77. The molar weights are measured downwards, and the temperatures to the right. The numbers placed beside the curves give the pressures.

The above facts show that when iodine vapour is heated, a transformation of the vapour I_2 into I takes place, according to the equation $I_2 = 2I$. Such a decomposition of one substance into simpler substances is called *dissociation*. From the fact that the decomposition increases with rise of temperature, it is to be concluded that heat is absorbed in the process, in accordance with the repeatedly expressed general principle of resistance to change. Since the second form would, under the same pressure, occupy double the volume of the first, and, therefore, if the volume is the same, would exert twice the pressure, the transformation of I_2 into $2I$ would, at constant volume, cause an increase of the pressure. From this fact it can be concluded, on the ground of the same general principle, that the decomposition will be promoted by diminution of pressure, since the decomposition opposes the latter. This conclusion is borne out by the experiments represented in Fig. 77.

compared with I_2, the substance I must be regarded as a new substance with different properties. Owing to the difficulty of investigation at such high temperatures, it has hitherto been impossible to determine these differences quantitatively except in the case of the density. It has, however, been stated that a change in the colour of the vapour has been observed.

Starch Iodide Elementary iodine in the pure state, whether in vapour or in solution, is, even of itself, distinguished by its strong colour. Still smaller quantities than can be detected by the colour of the free iodine can be detected by the colour of a remarkable compound which iodine forms with *starch*.

Starch is an organic substance (that is, a substance containing carbon, composed of carbon, hydrogen, and oxygen, which occurs very widely distributed in plants, collected chiefly in the seeds or the parent portions of the vegetable organism. It is prepared mostly from potatoes and from wheat, and is obtained in the form of a white powder which is insoluble in cold water, but in hot water swells up to a gelatinous mass. If much water be taken, say, a hundred times as much as the weight of the starch, a liquid is obtained which can be freed from the undissolved cell walls, and which then appears and remains liquid.

This solution of starch, now, has the property of yielding a fine blue colour with free iodine. This coloration is exceedingly strong. The very feebly brownish coloured solution obtained by shaking iodine with water, becomes of a dark blue colour with starch solution, and solutions somewhat richer in iodine are rendered opaque. The compound that is here formed, contains the iodine only very feebly united; it acts in almost every respect like free iodine, and it is therefore employed in many chemical reactions in which iodine is produced or used up, as an indicator for the first or for the last traces of

If a solution of starch iodide, as the blue substance is called, is heated it becomes colourless at a temperature a little below the boiling point, exhibiting only the feebly brownish colour of iodine. On cooling, the blue colour again appears, showing that the compound is again formed from its components.

This experiment can be rendered very clear if only the lower part of the colourless solution, obtained by heating in a test tube, is cooled by partially immersing the tube in cold water. Only this portion will then become blue, and as the cooled liquid is the specifically heavier, it will remain undisturbed at the bottom and the boundary is fairly abrupt. In proportion as the solution cools, the blue colour gradually moves upwards.

This colour phenomenon serves for the detection both of iodine and of starch, and has, for both purposes, a great value.

Hydrogen Iodide Iodine and hydrogen unite to form

hydriodic acid, which, in accordance with its formula HI, has the density 128. Like the other halogen hydracids, it is, at ordinary temperatures, a colourless gas. Its liquefaction, however, under atmospheric pressure, takes place even at -34.

The union of the two elements is still less stable than in the case of hydrogen bromide. If a mixture of hydrogen and iodine vapour in equal volumes be heated, only a portion of the mixture combines to form hydrogen iodide, the other portion remaining uncombined. This proportion, also, is not altered by adding platinum sponge; the total invariable state will only be very much more quickly reached. The point varies somewhat with the temperature; at 520, 76 per cent of the mixture combines.

Conversely, already formed hydrogen iodide, when heated, partially decomposes into iodine and hydrogen, the mixture finally having, indeed, exactly the same composition as before. In this case the presence of platinum sponge accelerates the decomposition just as in the former case it accelerated the combination, in conformity with the general law of catalytic acceleration.

In accordance with the formula

$$H_2 + I_2 = 2HI,$$
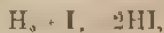
two volumes of the compound are produced from two volumes of the mixed gases; the reaction, therefore, takes place without change of volume. Now, we have just seen (p 234) that a diminution of the pressure promotes that reaction which, at constant volume, would be accompanied by increase of pressure. On attempting to apply this rule here, the difficulty arises that neither of the two possible reactions — neither the formation nor the decomposition of hydrogen iodide — would cause an increase of pressure. The conclusion to be drawn from this is that in this case change of pressure has *no* influence on the chemical equilibrium. This conclusion has been confirmed by experiment.

This case can be generalised, and we can enunciate the rule *If definite states are not altered by given processes, a change in these states has, conversely, no influence on the processes.* With the help of this rule, conclusions can sometimes be drawn which are as important as the rule is simple

Hydrogen iodide can be prepared, similarly to hydrogen bromide, by means of phosphorus and water, as well as by heating iodine and hydrogen in the presence of platinum. The reaction is in this case much less violent. Red phosphorus, water, and iodine can be mixed in the order given, in the proportions 1 . 4 . 15, without any considerable reaction taking place; on heating, hydrogen iodide is then evolved, and can be collected by downward displacement, as it is four times heavier than air.

On account of the readiness with which it decomposes, almost all

... cannot increase indefinitely, for it must reach its maximum when ... ation is complete.

As a matter of fact, measurements of the conductivity have shown ... there is a maximum for the strength of acids which cannot be ... Hydrochloric acid, even in moderately dilute solutions, ... mates to this maximum, and must, therefore, be designated as ... strongest acids. To the same class belong the other halogen ... with the exception of hydrofluoric acid, which is considerably less ... acid.

... dissociation of hydrochloric, hydrobromic, and hydriodic acids, ... as that of all other acids, increases with the dilution. In the ... table there is given the fractional dissociation at the ordinary ... rature (20), the dilution being expressed by the number of ... which 1 01 gm. of hydrogen is contained.

	HCl	HBr	HI	HF	Sulphuric Acid	Acetic Acid
	0 95	0 97	0 95	0 10	0 57	0 014
	0 98	0 98	0 98	0 26	0 74	0 09
	0 99	0 99	0 99	0 53	0 92	0 125

Whereas, therefore, the first three acids change only slightly with ... tion, the others do so to a large extent, and tend to assume the ... a value which is already almost reached by the former. *The ... the acids, the more nearly do they approach one another in ...*

These relations obey certain laws which we shall not consider, ... unto a later point

When we speak, therefore, of the *strength* of an acid, we mean its ... the fraction of the total amount which is in the form ... The conception applies, naturally, only to aqueous solutions. ... strength varies also with the temperature and the dilution, but ... the absolute values of the degree of dissociation are thereby ... the ratio of the different acids remains unchanged.

An approximate measure of the strength of an acid is afforded ... comparison of its conductivity with that of an equivalent ... of hydrochloric acid. Since at fairly great dilution, the latter ... materially fall short of complete dissociation, the conductivity ... acid referred to hydrochloric acid equal to unity, gives the ... of its hydrogen which is in the ionic condition, or the degree ... ciation of the acid. We have here, it is true, neglected ... conditions, still these cannot give rise to any considerable ...

Of the oxyacids of the halogens, chloric, bromic, iodic and per ... acids are dissociated to approximately the same extent as ... chloric acid. Hypochlorous acid, on the other hand, is very ... dissociated; the exact degree of dissociation, however, is ... unknown.

dilute hydrochloric acid, do not dissolve it to a much greater extent than water.

The answer to this question is that the iodine can combine with the iodidion of the hydriodic acid in accordance with the equation $I' + I_2 = I_3'$ to form *triiodidion* I_3', which is coloured brown. The combination does not take place completely, about half of the iodine remaining uncombined. Hence, about as much free iodine dissolves in the solution of dilute hydriodic acid as there is iodine already present in the form of iodidion. In more concentrated solutions, however, the solubility of the iodine is considerably greater.

From what has been said, it follows that iodine must dissolve to the same extent in the solutions of all metallic iodides capable of forming iodidion. This has been found by experiment to be the case.

These considerations can be generalised. When in dilute solution the solubility of a substance is increased by the addition of another substance, this is to be explained by the conversion of the solute into another compound, to an extent corresponding to the increase of the solubility, by the substance added. So much passes into solution that the uncombined portion amounts to about as much as it would do in the pure solvent ; the excess is in a state of combination.

The fact that this rule has been expressed only for *dilute* solutions is conditioned by the circumstance that additions alter the nature of the solvent and thereby influence the solubility. An example of this is to be found just in the case of iodine, which is dissolved more especially by concentrated solutions of hydriodic acid and of iodides, in much larger quantities than it ought to be from the above cause alone.

In the brown solutions of iodine in iodides, therefore, only a small portion of the iodine can be regarded as existing in the free state, namely, an amount not greater than is dissolved by water (p. 242). Still, the solutions mostly behave as if all the iodine dissolved were free. This is due to the fact that in proportion as the free iodine is removed by any reaction, fresh iodine is formed by a splitting up of the ion I_3, into $I' + I_2$. This process takes place so quickly that there is at no time a complete absence of free iodine so long as any triiodidion, I_3', is still present.

It can be seen that the iodine is indeed combined and not free, by shaking a solution of iodine in carbon disulphide with a large quantity of hydriodic acid or potassium iodide solution. Although no appreciable amount of iodine can be removed from this solution by pure water (p. 235), the violet colour in this case for the greater part disappears, and the iodine passes into the aqueous solution with a brown colour.

226. Oxygen Compounds of Iodine. On dissolving iodine in caustic soda solution, sodium hypoiodite or *hypoiodesium*, IO, is first formed in accordance with the same scheme as in the case of the other

...such a nature that ions are removed by it, and that it continues so long as ions of the particular kind are present, it will depend on the total amount of all possible ions. By means of this rule each separate case can be decided.

Thus, the precipitation of chloridion by silver solution is, evidently, a process which gives the amount of the *potential* ion. When the silver is present in sufficient amount, the process does not cease until all the chloridion, not only that present at the beginning, is exhausted. For the chloridion is removed from the solution by the precipitation of the silver chloride in the solid state, and the process will continue so long as chloridion can still be formed from the associated chloride present.

The determination of the electrical conductivity, however, gives information only as to the amount of the *ions really present* or the free ions, for by such a measurement no ions, or only a vanishingly small amount of ions, are used up.

From this it is clear that in order to measure the state of dissociation or, generally, the concentration of any ions, only those processes are directly applicable by which the amount of the ions is not, or is only very slightly, altered.

The Dissociation of Salts.—Whereas in the case of the acids and, as we shall find later, to a certain extent also in the case of the bases, great variety exists in the degree of dissociation,—all possible values, in fact, occurring,—the behaviour of the neutral salts is much more uniform. Almost all these are dissociated to a fairly large extent, and only in quite exceptional cases are salts found which show deviations in this respect.

Except in these special cases, therefore, it will not be necessary in the case of chemical reactions between salt solutions to refer specially to the state of dissociation. The actual conditions will be represented very closely if we assume that all the salt present is dissociated into its ions, and that the reactions take place exclusively between the ions.

An important conclusion which can be drawn from this is that when different salt solutions are mixed with one another, the liquid thus produced will always be of the *same* nature, *if it contain the same ions in the same amount*, no matter what the arrangement of these ions was in the salts used for the preparation of the solution. A mixture of equivalent amounts of sodium chloride and potassium iodide can in no respect be distinguished from one prepared from the corresponding amounts of potassium chloride and sodium iodide.

Further, since the state of the substances present is not altered by mixing the two solutions—for the substances were present as ions to start with and are so also after the mixing—none of those processes take place by which the occurrence of chemical change is characterised. There occurs *no change either of the temperature or of the volume or*

This oxide also dissolves in water, but is thereby transformed once into the acid, combining again with the elements of water.

If the oxide be still more strongly heated, it decomposes into oxygen and iodine, which is recognised by its violet colour.

If iodic acid and hydriodic acid be brought together, they speedily act on one another, with formation of water and iodine—

$$H^{\cdot}IO_3{}' + 5H^{\cdot}I' = 3H_2O + 3I_2$$
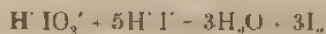
This reaction does not occur on bringing potassium iodide and iodate together, since the hydrion necessary for the formation of water is wanting. If this, however, be added in the form of some acid, iodine immediately separates out. This reaction can be used as a sensitive indicator for the presence of hydrion. In the case of strong acids or high concentration of hydrion, the reaction proceeds so rapidly that the various steps cannot be followed; with very weak acids, however, it can be seen that the reaction is not complete in a moment, but that it requires time.

227. Periodic Acid. —If sodium iodate be subjected to the action of specially energetic oxidising agents, it takes up a further combining weight of oxygen and passes into the salt of *periodic acid*, which in solution forms *periodanion*, $IO_4{}'$. The periodic acid corresponds to a certain extent to perchloric acid, but differs from it by the fact that in the pure state it is a solid substance, the composition of which is not represented by HIO_4, but by the formula H_5IO_6, containing two combining weights of water more. On careful heating, periodic acid also loses water and forms an anhydride I_2O_7; by careful dehydration an intermediate substance of the composition HIO_4 can be obtained.

The behaviour of periodic acid towards bases is different from that of the acids hitherto discussed. Besides the salts of the formula MIO_4, corresponding to the salts of perchloric acid, periodic acid forms salts with three and five combining weights of metal. The formulæ of these are obtained by imagining one or two molecules of water added to the formula HIO_4, and the hydrogen of the compound thus formed replaced by metal. In other words, there exist besides the acid HIO_4, also the acids H_3IO_5 and H_5IO_6. Acids such as these which contain several combining weights of hydrogen replaceable by metals, are called *polybasic* acids. They contain polybasic anions; in the present case the trivalent ion $IO_5{}'''$, and the pentavalent ion $IO_6{}'''''$. We shall discuss the relations of these acids later, with the help of a simpler and better known example (Chap. XII)

228. Chlorides of Iodine. –In the experiment on the decomposition of hydrogen iodide with chlorine described on p. 237, it is observed that if the chlorine is present in excess, the iodine does not *separate out* in the usual dark lustrous crystals, but that a reddi

... liquid of the appearance of bromine, and also reddish-yellow ... are produced Both these are new substances formed by the ... action of chlorine with iodine.

The red-brown liquid has the composition ICl, is called iodine ... chloride, and is formed with extreme readiness by passing ... one over iodine. Under the influence of the chlorine, the iodine ... and by starting with weighed quantities the experiment can ... interrupted when the increase of weight corresponding to the ... has taken place.

This substance can be solidified by cold, and is obtained in two ... one of which melts at 14, the other at 27. Of these two ... the one with the higher melting point is stable; the other ... however, is produced more readily by spontaneous solidification ... the liquid is cooled down. If a little of the higher melting form ... ought into contact with the form of lower melting point, the latter ... into the former, the reverse transformation never takes place. ... liquid cooled below 14, in the neighbourhood of which ... the liquid does not spontaneously solidify, the one or the ... form separates out, according as crystals of the one or other form ... added

The relations described here are found in the case of a large num ... substances. Besides the liquid form, only one kind of which ... present, there are often several solid forms possible, each of ... has its special melting point. The form with the lower melting ... always unstable with respect to the form of higher melting ... that it can pass into the latter, whereas the reverse transfor... never occurs This phenomenon is called *polymorphism*, and ... different forms polymorphic forms.

Besides the iodine monochloride, there is another compound, *iodine* ... ICl₃ It is easily obtained by passing an excess of chlorine ... iodine, the brown liquid which is first produced soon solidi... to red-yellow crystals, which cannot be melted at ordinary ... as they previously decompose into chlorine and vapour ... the monochloride. If the decomposition be hindered by an ... of pressure, a melting point under 16 atm. can be observed

Both compounds are decomposed by water with formation of ... acid, iodic acid, and free iodine Still the trichloride ... dissolve partially in water without decomposition, and to be ... on mixing concentrated solutions of iodic acid and hydrogen ...

Besides these compounds, there exist compounds of iodine and ... and of iodine and fluorine. These will not be discussed here

... general, only for the behaviour of the substances in the neighbour... At temperatures above the ... at a greater distance below the ... can become reversed

R

By measurements of the electric conductivity of aqueous solutions of hydrofluoric acid, it is found that it is much less dissociated into ions than the other halogen hydracids. A normal solution, containing one mole in the litre, is rather more than 3 per cent dissociated whereas the other halogen hydracids are dissociated to 80 per cent. Hydrofluoric acid is, therefore, a considerably weaker acid than the others.

In its general behaviour also, fluoridion differs essentially from the other halogen ions. With silver solutions it gives no precipitate; on the contrary, silver fluoride is readily soluble in water. On the other hand, *calcium* fluoride is a difficultly soluble substance, whereas the other halogens form extremely soluble compounds with calcium.

233. The Strength of Acids.—The new acids which have just become known to us, give occasion to some further general considerations in amplification of those made on p. 187. Acids possess a number of common properties which clearly manifest themselves in the colour reactions with litmus and similar colouring substances, and which can also, by means of numerous other reactions, be quantitatively determined.

This similarity in action is appropriately attributed to the presence of the same substance, hydrogen. In the first place, now, we learn that the acid properties were by no means exhibited by all hydrogen compounds; all hydrogen, therefore, is not of this nature. The acid hydrogen is characterised chemically by the fact that it can be replaced by metals, as has already been explained on p. 187.

It would, therefore, be expected that those quantities of different acids which contain equal amounts of hydrogen (hence called equivalent), would also exhibit equal acid actions. In certain respects this is the case; thus, such amounts of different acids always neutralise equal amounts of the same base (p. 189), and evolve with metals, as magnesium, equal quantities of hydrogen. On the other hand there are other reactions in which the different acids behave differently. For example, on introducing pieces of zinc of equal size into equivalent solutions of hydrochloric acid, sulphuric acid, and acetic acid, the metal acts, it is true, on all the acids with evolution of hydrogen, and the amount of hydrogen which is *ultimately* evolved is the same in all cases; the *velocity*, however, with which the reaction takes place in the different cases, is very different. It is greatest in the case of hydrochloric acid, less in the case of sulphuric acid, and very small in the case of acetic acid.

" These differences can be clearly shown by placing the acids with the zinc in small flasks fitted with gas-delivery tubes, and collecting the evolved hydrogen in three cylinders of equal section placed side by side and standing over water (Fig. 78). The differences are quite distinct after 5 to 10 minutes if equivalent normal solutions, i.e. solutions con-

.01 gm hydrogen in the litre, are used. In order to be
...ent of impurities which may be present in the zinc, and which
...e a difference in the evolution of gas, equal quantities of a
...lution of copper sulphate is added to each of the solutions
...ution thereby becomes rapid and uniform, and the collection
...s is not begun until somewhat later.

...llel with these, there run other differences which have refer-
...e velocity of chemical processes and the equilibrium relations.
...ch cases, several
...b will be dis-
...ter, the acids are
... in the same
...o that we must
... that there are
...differences attach
...the acids them-
...ed independent
...nature of the re
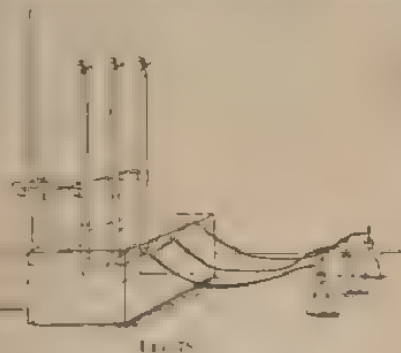
Difference in
...ytic Dissocia-
...It has been al-
...entioned that the acids in aqueous solution are electrolytes,
...duct the electric current with decomposition. If, now, the
...*equivalent solutions* of the different acids be compared, it
... that in this respect also the acids form the same sequence as
...case of their last mentioned properties. Hydrochloric acid
... best, sulphuric acid less well, and acetic acid much worse.
...ent is found in every detail, and is present also in the numerical
... It follows from this that we are dealing with the operation of
... cause, and any interpretation of the described relations must
...unt of all these properties.

...power of conducting the electric current was attributed (p. 200)
...al condition of the participating substances, the ionic condition
...which the components exist in a certain degree of independ-
... one another, or of freedom, and this finds its expression just
...power of transporting opposite electricities in opposite directions.
... ionic independence is proved by the identity of the chemical
... of an ion, independently of the presence of other ions (p. 189).
... great differences in electrical conductivity of equivalent solu-
...cids, and the corresponding differences in chemical reactivity,
... attributed to the fact that *not the whole amount but only a*
...*y the acid present is in a state of free ions.* By this portion
... electric conduction is performed, and on it depend the velocity
...equilibrium in the case of the reactions of the acids. Of the
...hydrogen of an acid, then, a portion is present in the state of

value   The equality of the numbers in the case of the former ac
is due to the fact that these are to a large extent dissociated i
ions in the dilute aqueous solutions used ; the heat of neutralisa
is, therefore, equal to the heat of formation of water from its c
hydrion and hydroxidion, as was shown on p. 203.   The greater he
neutralisation in the case of hydrofluoric acid is connected with
slight dissociation in aqueous solution (p. 203), and, indeed, it can
concluded that the dissociation of hydrofluoric acid into its ions tak
place with *evolution* of heat.   For we can regard the neutralisation
this acid by caustic soda as if the acid first dissociated into ions a
the hydrion then combined with the hydroxidion of the soda to f
water, while the fluoridion and the sodium remain side by side in s
solution, in accordance with the circumstance that sodium fluor
being a neutral salt, is, in aqueous solution, dissociated to a la
extent into ions (p. 249).   The total heat evolution consists, therefor
of the heat of dissociation of the hydrofluoric acid and of the heat
formation of water from hydrion and hydroxidion.   The latter reactio
gives a heat development of 57 k_j ; the excess, 68 − 57 = 11 k_j, is, there
fore, the heat developed in the dissociation of hydrofluoric acid in
ions.[1]

On comparing the heats of formation of the halogen hydrides wi
the known chemical reactions which occur between these and the tw
halogens, it is found that there take place between them those reaction
which are accompanied by an evolution of heat.   Thus, chlorine li
places bromine and iodine from their hydrogen compounds, and, i
aqueous solution, an amount of heat equal to 164 − 118 = 46 c or
164 − 55 = 109 k_j is set free.   Very nearly the same evolution of hea
is found in the case of the salts of the halogens, because the heats o
neutralisation of the three acids with most bases are equal, and thei
influence is, therefore, cancelled.

* Similar relations can be frequently observed, and have given ris
to the idea that one can predict the direction of the corresponding
chemical reaction from the sign of the "heat effect," by which ter
there is understood both the development and the absorption of hea
Such a theorem would contain the assumption that only those chemica
reactions can take place which develop heat

* Now, although, as a matter of fact, the majority of the know
chemical reactions take place with development of heat, there are n
a few known in which the opposite, the absorption of heat, occurs a
that the temperature of the reacting substances falls spontaneousl
The attempts to attribute the absorption of heat in such cases t
secondary reactions or to changes of the physical state, have failed, fo

[1] Since the hydrofluoric acid is somewhat dissociated, and also the sodium fluorid
contains some undissociated salt, this calculation does not give the whole amount of
heat, but only a part. This circumstance changes somewhat the numerical value of the
result, but not its general character.

difference between primary and secondary reactions is just as ... as that between physical and chemical changes of state. On ... contrary, the conclusion was unavoidable that such a theorem can ... established, since it is in contradiction to the facts

If we recall the statements made on p. 211, we see that it is the ... of the *free energy* that determines a chemical reaction. The ... of the heats of formation, however, are a measure not of the ... of the *free* but of the *total* energy. For this reason, direct ... cannot be drawn from the one set of figures with regard to ... .

So far, however, as determinations have been possible, the differ ... between the free and the total energy are, in general, not great. ... conclude, therefore, with a certain degree of probability, that ... cases where the differences of the total energy are large, the ... ding differences of the free energy will have, if not the same ... at least the same sign. With this reservation, it will certainly ... e to draw conclusions as to the direction of the reaction from ... of the heat of the reaction. In all cases, however, in which ... of reaction is small, the conclusion becomes doubtful.

One case in which a reaction takes place spontaneously with ... of heat, can be at once discussed on the basis of the table ... . On adding a solution of hydrochloric acid to a solution of ... fluoride an absorption of heat of $10 k_j$ occurs. This is due to ... that in this case the ions of hydrofluoric acid, fluoridion, and ... come together. Hydrofluoric acid, now, is slightly dissociated ... , its ions, therefore, must combine whenever they come ... . This combination, however, is accompanied by an *absorp* ... heat, for the *dissociation* of hydrofluoric acid into its ions, ... we have just seen, *develops* heat. Since the other ions, viz. ... and sodion, remain unchanged in the experiment, no other ... a heat effect exist, and the reaction takes place, as observation ... , with absorption of heat.

Since in this reaction undissociated hydrochloric acid is chiefly ... , the process was formerly interpreted as if the "weaker hydro- ... acid is displaced from its compound with sodium by the stronger ... acid." As the above consideration shows, the impelling ... lies not so much in the hydrochloric acid as in the hydrofluoric ... the slight dissociation of which conditions the reaction. This ... true, take place only in the presence of a "strong" acid, for ... an acid is one that is to a large extent dissociated into its ions, ... only such an one, therefore, can yield the requisite amount of ...

235. Actual and Potential Ions. Since hydrion has just been designated as the substance which manifests the typical acid reactions, and it has further been shown that in solutions of acids and of moderate concentration only 1 to 2 per cent of the hydrogen is present in the ionic form, one might suppose that on titrating with caustic soda the red colour of the litmus would disappear after this hydrion had been converted to water by the addition of a few per cent of the equivalent of alkali. This is not the case. On the contrary, we have seen that the different acids require exactly as much alkali as corresponds to their equivalent (p. 189). For the process of neutralisation, therefore, it is a question not merely of the hydrion but of all the acid hydrogen, whether it is present as ion or not.

This apparent contradiction is removed when we consider more carefully what is the course of the process of neutralisation. On addition of caustic soda, the ions H' and OH' in the first place act on another and form water. There exists, however, a chemical equilibrium which depends on the proportions of the participating substances, between the portion of the acid which has passed into ions and the undissociated portion. If one of the substances is removed, that reaction must immediately take place by which it is again replaced. In proportion, therefore, as the hydrion is removed by combination with the hydroxidion, a *fresh amount* must be produced by the dissociation of the still undissociated portion. This new reaction can take place as long as there is undissociated acid present, but when this is used up the hydroxidion will no longer be bound, and the blue colour of litmus must appear.

Now all processes between ions proceed, as experience shows, so quickly that it has hitherto never been possible to measure their velocity. In the case of our experiment, therefore, we see only the final result, and on titration with caustic soda we do not obtain the amount of hydrion present at the preliminary moment, but the amount of all the hydrion that can be formed from the substances present, not the ... amount of the ions, but the *potential*.

The same holds for the action of the metals, e.g. zinc, on the acids, where the total amount of the possible hydrion is ultimately evolved as hydrogen gas. In this case, however, the velocity is measurable, and it is found to be all the greater, the greater the concentration of the hydrion actually present. The same is found in all processes which depend on the hydrion and which proceed with measurable velocity.

The question as to the conditions under which only the actual, and under which the potential ions are to be considered, can be answered to the effect that the former are all-important when the amount of the ions present is unaltered, or is altered only in an incomparably slight degree, by the process. If, however, the process

short time, the surface crust of solid sulphur be broken and
the portion poured out, the crystals which have been formed
exposed and a large number of them will be found on breaking
of sulphur

a short time after they have been formed, these crystals are
amber yellow colour and can be bent slightly without breaking.
following day, the appearance of the crystals has considerably
d, they have assumed the lemon yellow colour of the ordinary
phur and have become brittle.

Crystallisation from Solution.—If, on the other hand,
be dissolved in a suitable solvent, the best being carbon
(p. 252), and the liquid be allowed to evaporate, crystalline
also separates out. This, however, has the octahedral forms
sulphur and undergoes no change on being kept at room
are

however, the octahedral sulphur (natural or artificial) be heated
eratures of over 100, without being melted, it also becomes
brittle.

The Regions of Stability.—The above phenomena are due
fact that to each of the two forms of sulphur there corresponds
a temperature in which the one form is stable, but in which
form is unstable and is converted into the former. The
the octahedral sulphur extends from low temperatures up to
the prismatic sulphur from 96 to 120, its melting point.
prismatic sulphur is unstable and passes into octahedral,
96, octahedral sulphur is unstable and passes into prismatic.
relations show a very great similarity to the reciprocal trans-
of ice and water, or, generally, to fusion and solidification.
cases so also in the present, there is a temperature above
only the one form, and below which only the other form, is stable
this point, therefore, the one form passes into the other.
this one temperature can the two forms exist together

Influence of Pressure on the Point of Transition.—
that we are dealing here with a single substance we shall
accordance with the phase law (p. 173), that there will be
temperature and one definite pressure at which three phases
side by side. At 96, these phases are octahedral sulphur,
sphur, and sulphur vapour. If we exclude the vapour, the
which determines a definite, very small pressure, the tem
of equilibrium of the two forms of sulphur *varies with the*
The temperature of transition, indeed, is raised by pressure,
the prismatic sulphur occupies a larger volume than the
ral. However, as in the case of ice and water (p. 132), a very
ressure is here necessary in order to effect a slight shifting of
perature of equilibrium. For the rest, the two forms of sulphur
as two *independent substances.* Not only the crystalline forms,

S

but also the density, the power of refracting light, the melting point, and all other properties, are different. The density of prismatic sulphur is 1·96, that of octahedral, 2·07

The prismatic crystals obtained from the fused sulphur, and which have become opaque, have the density 2·07, the density of the octahedral form. This is the simplest proof that they have really become converted into octahedral sulphur. We have the reverse phenomenon in the case of the octahedral sulphur transformed by heating.

246. **Suspended Transformation.** Just as water can be cooled below 0 without solidifying to ice, the temperature of transformation of the two forms of sulphur can be overstepped from both sides. If octahedral sulphur be rapidly heated, it melts at 115 , which is its true melting point. If, however, it be slowly heated, so that it has time to undergo transformation, fusion is observed at 120 , the melting point of prismatic sulphur.

247. **Enantiotropy and Monotropy.**—A comparison of the behaviour of the two forms of sulphur here described with the two chlorides of iodine (p. 240), reveals an essential difference. Whereas in the case of the chlorides of iodine, only the one form is stable and the other is unstable, in the case of sulphur, both forms are stable each one being stable in its own range of temperature and unstable in the range of temperature of the other.

The difference lies in the fact that in the case of sulphur, the melting point of the more readily fusible form is above the temperature of transition at which the stability of the two forms changes, whereas in the case of the chlorides of iodine, the less stable form melts before the temperature of transition is reached.

Substances like iodine monochloride, which can undergo transformation only in one direction, are called *monotropic*, and those which, like sulphur, can change in both directions, *enantiotropic*.

248. **Other Forms of Sulphur.**—Other crystalline forms of sulphur, differing from the two already described in form and in other properties, can be obtained by strongly heating small quantities of sulphur and allowing it to cool rapidly. They are, however, all *unstable* with reference to the octahedral and prismatic sulphur, and according to the temperature, pass into the one or other of these. In respect of these forms, therefore, sulphur is *monotropic*.

We need not here describe these forms in greater detail, as they are only of rare occurrence.

Sulphur has also been known for a long time in the form of *flowers of sulphur* and *milk of sulphur*. These two kinds of sulphur are not special forms in the scientific sense, but represent only peculiar states of division of sulphur and consist chiefly of octahedral sulphur, at least after being kept some time

Flowers of sulphur is produced in the distillation to which sulphur

... for the purpose of purification (p. 263). So long as the densing chamber is cold, the vapours on falling down solidify in ... crystals, and sulphur is obtained in the form of a yellow powder ... has been known from the time of the alchemists as flowers of ... The powder almost always contains, however, small quanti-... of amorphous sulphur.

By the name *milk of sulphur* there is denoted a very finely divided ... of sulphur which is precipitated from aqueous solutions in ... reactions. These processes will be described later. In this ... sulphur is obtained in such a fine powder that its yellow colour ... almost invisible, and it emits almost entirely white surface ... p. 15). On account of its finer state of division and corre-... large surface, this form of sulphur more readily undergoes ... change, on this fact depends the application of milk of ... in medicine. Milk of sulphur does not differ chemically from ... ary sulphur.

Liquid Sulphur.—As already mentioned, prismatic sulphur ... at 120 ; it thereby changes into a light yellow, mobile liquid ... on cooling, solidifies at once to prismatic sulphur. In small ... however, and by excluding particles of solid sulphur, liquid ... can be strongly supercooled. It then exhibits properties quite ... to those of supercooled water.

If the melted sulphur be further heated, it exhibits very remark ... phenomena. Whereas, in general with rise of temperature, the ... fraction of liquids decreases, we find the opposite behaviour ... case of liquid sulphur. The higher the temperature rises, ... more viscid does it become. At the same time it becomes ... in colour, and at 250 it passes into a dark red mass, which ... viscous that the vessel may be turned upside down without ... out. On further heating, the mass again becomes more ... without, however, losing its dark colour. At 450 the ... is again quite liquid and boils, passing into a red-brown ...

... heated sulphur, on being allowed to cool, again passes through ... conditions in the reverse order ; it first becomes viscid, then ... again and light in colour, and solidifies, finally, in prismatic ...

Amorphous Sulphur.—Strongly heated sulphur behaves ... differently on being rapidly cooled, as *e.g.* by pouring it into ... water. It then assumes a viscid character like that of elastic ... rubber, and is called *amorphous* sulphur.

... designation denotes that the sulphur in this form is not ... although it exhibits, to a certain extent, the properties of ... body. On the other hand, it can be regarded as a liquid with ... internal friction. This view is supported by the fact that amor ... solid *substances, on heating, exhibit a continuous* transition into

the liquid state; no definite melting point can be observed, but the internal friction continuously decreases. All the other properties also change continuously, until a state with the characteristic properties of a liquid is produced.

The amorphous, viscid sulphur does not remain in this condition at ordinary temperatures. After some days, sometimes also only after a fairly long time, it changes into an opaque, brittle mass which, from its density, proves to be octahedral sulphur.

We must conclude from this that at ordinary temperatures, the amorphous sulphur is a *less stable* form than the octahedral. As a matter of fact, the latter is the only form of sulphur which is stable at room temperature; all the other forms, of which there are several besides those already mentioned, pass in course of time into octahedral sulphur. This is, accordingly, the only form which is found in nature.

The fact that the rapidly cooled sulphur does not immediately pass into that form which is stable at the existing temperature, but that it first assumes a less stable form, is a special case of the general law that when changes of state take place those forms are usually produced which are the least stable of the forms possible under the existing conditions (p. 210). The forms first produced afterwards change into the more stable ones, when this becomes possible. The velocity of the transformation varies greatly, and the transformation may take place in the fraction of a second or may last for years or centuries. The changes in the properties of liquid sulphur with the temperature which have been described, lead to the conclusion that sulphur, in the liquid as in the solid state, can assume different allotropic forms. It has hitherto not been possible to prepare these forms in the pure state and to characterise them.

* 251. **Experiments** On account of the variety of its forms, sulphur is specially well adapted for a study of the reciprocal relations and conditions of stability of different forms of the same substance. These relations can be observed in a very instructive manner by introducing a small piece of sulphur into a tube about 2 cm. wide, exhausting the tube, and sealing it off.

On slightly heating the spot where the sulphur is situated, the latter gives off vapour, and on the colder parts of the tube drops (not crystals) of sulphur are deposited, although the temperature is there much below the point of solidification of sulphur. The less stable, liquid form, therefore, is first produced

If the tube be allowed to remain in this state for some hours and the deposit of drops be examined with a lens, the following appearance is found Many of the drops still remain liquid, as can be seen from their transparency; others have solidified to crystals. Where a crystal has formed, it is quickly encircled by a clear ring, the surrounding drops disappearing. This is due to the fact that the vapour pressure of the *crystallised* sulphur is *smaller* than that of the *liquid* at the same tem-

ture. For the crystalline form is the more stable of the two, and
t, in accordance with the considerations put forward on p. 135, also
e the smaller vapour pressure. Sulphur distils, therefore, from the
e to the crystals, and the former disappear from the neighbourhood.
Occasionally, also, other regions are seen in the tube where no
tal has formed, but where, nevertheless, the formation of a "halo"
rual. On closer examination of such a spot, it is seen that the
re of the clear space is occupied by a drop which is *larger* than those
ounding it. In accordance with the reasoning just applied, we
t conclude that larger drops of sulphur have a smaller vapour
sure than small ones. This also is the case, and follows from
ectly similar considerations.

Thus, on bringing two drops into contact, they unite with a cer-
force and form a single drop. This union takes place in
equence of the surface tension of the liquids, by virtue of which
quid tends to assume that shape which has the smallest possible
surface. In the case of large masses of liquid, the surface tension
small compared with the influence of gravity; in the case of
ll quantities of liquid, however, it is the determining factor and is
cause of the spherical shape of the drops.

Now, the surface of the sphere formed by the fusion of two drops
maller than the sum of the two spherical surfaces before the
n. Since the surface tension tends to diminish the surface, there
ts also the tendency to form a large drop from several small ones.
tendency exerts itself in all ways in which the object can be
ined. Since it can also be attained by distillation, the cause of
distillation, viz. the difference of the vapour pressure, must be
that this tendency is given effect to. The vapour pressure of
ll drops, therefore, must be greater than that of large drops, as
riment also shows.

If the tube with the deposits of liquid and solid sulphur at various
s be allowed to remain undisturbed for a fairly long time, the
sits all disappear, and there is only the large piece of sulphur
in the tube, which has now become clear. All the sulphur has,
efore, distilled over to the large piece. The cause is the same as
re, for solid substances also have a surface tension, and, therefore,
e exists the tendency to make the surface as small as possible or
pieces as large as possible.

For the *solubility*, exactly the same considerations hold as for the
our pressure. If a glass plate, such as is used as an object glass
microscopic purposes, be held over heated sulphur until a depo
been formed on it, and if a drop of water (or of glycer
d evaporation) be placed on this and the whole co
r-glass, exactly the same phenomena of "halo" f
consumption of the less stable forms by the mo
rved. This experiment serves at the same time to

the solubility of sulphur in these liquids, a solubility that is so small that it has not been possible in any other way to measure it.

Applying these considerations to the conditions of transformation of the octahedral and prismatic sulphur, we can draw the following conclusions. The solubility of the former in any solvent must, below 96°, be smaller, and, above 96°, be greater, than that of the prismatic. Consequently, the solubility at 96°, the point of transition, must be the same for both forms. All this has been confirmed by experiment.

Since the considerations on which the conclusions are based are general, the law can be enunciated for all allotropic forms that the less stable forms must be more soluble than the more stable, and that at the point of transition the solubility of the two must be equal. Useful application of this law can be made in cases where the transformations are difficult to observe for the purpose of distinguishing the stable from the unstable forms.

252. **Sulphur Vapour.**—A similar variety of conditions is shown by sulphur in the vaporous, as in the solid and liquid form. At temperatures in the neighbourhood of the boiling point, the molar weight of sulphur vapour is 220; the higher the temperature is raised, the smaller does the molar weight become, until at 1000° it has fallen to 64, and at still higher temperatures it retains this value. These numbers are for atmospheric pressure. If the vapour of sulphur is investigated under smaller pressures, it is found that at a given temperature the molar weight is all the smaller the lower the pressure. This variability also ceases when the molar weight reaches the value 64. Sulphur vapour, therefore, follows neither the law of Boyle nor that of Gay Lussac, and only when the molar weight has become equal to 64 does it behave in accordance with these laws.

A similar behaviour has already been met with in the case of iodine (p. 234), and the same interpretation of the phenomena can be applied in this case, i.e. the vapour of sulphur exists in several forms with different molecular weights. Since the combining weight of sulphur is 32, the formula S_2 must be ascribed to the vapour which is stable at the high temperature and low pressure. With regard to the more dense form, the present case is more difficult than that of iodine, in so far as no region is known in which the density is constant. Even at the boiling point of sulphur we are in the region of variable vapour density. Since the highest observed value of the density amounts to 230, we can only conclude that the denser vapour contains more than six combining weights, or that in its formula S_n, n is at least greater than 6.

From determinations of the molar weight of *dissolved* sulphur in different solvents (cf. p. 158), the formula S_8 has been found for it. It can therefore be assumed with some degree of probability that the denser sulphur vapour also has the formula S_8, and that the vapour of variable density consists of a mixture of S_2 and S_8. Nevertheless, if

probable that other kinds of sulphur vapour S_n, where n is a whole number between 8 and 2, more particularly S_6, are also present.

With reference to the law set forth on p. 234, it follows as a necessity that on diminishing the pressure the less dense form of the vapour S_2 should be formed at the expense of the more dense S_6. From the fact also that this transformation is brought about by elevation of temperature, it can be concluded that the transformation from S_6 to S_2 takes place with absorption of heat.

253. Purification of Sulphur. — Use is made of the changes of state which sulphur undergoes, for the purpose of purifying it. As found in nature, it is usually mixed with other minerals, clay, and sand. In Sicily, the sulphur ore is piled up in a heap furnished with air channels, like the wood pile for the burning of charcoal, and is set fire to. The heat produced causes the sulphur to melt, and this flows away in a fairly pure condition, leaving the difficultly fusible impurities behind. By this method a loss of sulphur is incurred owing to the combustion of a portion of it, but this is by far the cheapest means of generating the heat necessary for the melting of the sulphur.

To completely free the already fairly pure sulphur so obtained from all non-volatile impurities, it is *distilled* from iron retorts, and the vapours are led into large chambers of mason work. At the commencement of the distillation these chambers are cold, and the sulphur vapours condense to a fine powder of sulphur particles. These are, at first, amorphous (cf. p. 259), but soon pass for the greater part into the crystalline condition. The powder is in part collected and is placed on the market under the name of *flowers of sulphur* (p. 258). On continuing the distillation the temperature of the chamber rises above 120°, and the sulphur then collects in it in the *liquid* state.

The liquid sulphur can be run off through an opening at the bottom of the chamber. It is collected in wooden moulds, in which it solidifies in rods of a slightly conical shape known as *roll sulphur*.

* B. Crystals

254. General. — The two known forms of solid sulphur differ not only in density and other properties, but also very materially in the form of their crystals, and the general question arises, therefore, as to the laws of crystalline form. All the more importance attaches to this question from the fact that the crystalline form is a property of almost all solid substances, and constitutes a very important means of describing and identifying these.

In the first place we draw the distinction between the two conditions of solid substances, the *amorphous* or formless, and the *crystalline* or formed. Since, however, the outward shape can be changed at will, some other more general characteristic must be sought for by means of which the two conditions can be distinguished.

The essential nature of crystalline bodies is found in the fact that their properties vary in a manner depending on the *direction in space*. For example, a ball of glass and one of octahedral sulphur, on being warmed, will behave differently. Whereas the glass ball remains a *sphere*, only increasing somewhat in size, the ball of sulphur passes, on being warmed, into an *ellipsoid*, the axes of which have a simple relation to the shape of the crystal from which the ball was cut.

Another example is furnished by the conduction of heat. If a glass plate be covered with a layer of wax and the point of a hot metal cone be placed on this, the wax is melted in the form of a *circle*, because the heat is distributed equally quickly in all directions. If the same experiment be carried out with plates cut from crystals, the melting takes place not in circles but in *ellipses* whose axes have different relative lengths according to the position of the plate in the
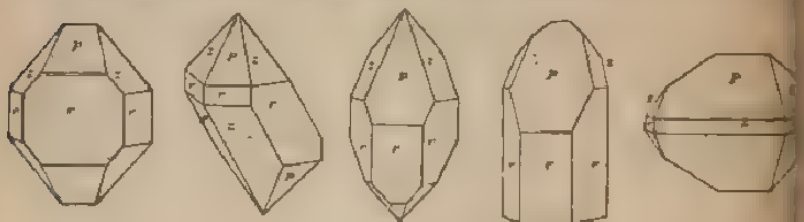
Fig. 80.

original crystal, and likewise stand in a definite relation to the shape of the crystal.

255. The Crystalline Forms. — By the name *crystal*, one is accustomed to think, in the first instance, of the regular forms which substances assume on passing into the solid state, and which can so often be observed in such exquisite beauty in the case of naturally formed solid bodies. The examples discussed teach that these forms are merely a definite expression of a much more comprehensive regularity. The forms are only an expression of the general fact that in crystals all properties which can be brought into relation with the direction in space undergo regular variation with this direction. Of the properties which concern us here, the most important is certainly the external shape, since it is, on the one hand, the one which first forces itself on the observation, and, on the other hand, exhibits the most manifold variety to be met with in the case of crystals.

Crystalline forms have the general property that they are bounded only by plane surfaces. If one examine, however, a group of simultaneously formed crystals of the same substance, *e.g.* a cluster of quartz crystals, it is soon seen that the appearance of the individual crystals is very varied, the outlines of the bounding planes being quite different. All the same, these various crystals (Fig. 80) preserve a *certain relationship* of form, which at once forces itself on one's notice.

Closer investigation shows that although the outline and the size of the faces which bound the crystals change, it is always possible to place the different crystals that *to every face of the one there stands a face of the other parallel to it.* From this it follows that the *angles* at which the various corresponding faces of two crystals meet, *are always the same.* Owing to one or other of the faces being formed relatively near or relatively far from the middle point of the crystal, the faces cut one another differently, but the angles between them remain the same.

Further, a cursory examination shows that the crystals are *symmetrical* structures. By this there is understood that different faces occur in a crystal, which are similar to one another and are repeated in a regular manner. Thus, for example, the snow crystals figured on p. have the property that each may be regarded as consisting of three similar parts arranged round the centre at angular distances of 120°.

256 The Symmetry of Crystals.—All the regularities exhibited by crystals can be deduced on the basis of the conception of symmetry. Three kinds of symmetry are to be distinguished. The first is that which exists between an object and its mirror image; the plane of the mirror is called the *plane of symmetry* of the structure.

A second kind of symmetry arises by rotating an object round a finite axis through an angle equal to a simple fraction of the total rotation, and repeating the rotation until the object again reaches its original position. According as this angle is $\frac{1}{2}$, $\frac{1}{3}$rd, $\frac{1}{4}$th, or $\frac{1}{6}$th of the total rotation, we speak of a binary, ternary, quaternary, or senary axis of symmetry. (Other grades, such as quinquenary, septenary, or higher, are not possible in crystals.)

The third kind of symmetry arises from a combination of the two just described, by *rotation and reflection.* If the object is brought into its next position by a rotation followed by a reflection, so that by repeating this process a number of times it again comes into its original position, such a structure possesses the third kind of symmetry. For our studies, it is essentially the first two kinds of symmetry, reflection and rotation, that are of account.

By using the three kinds of symmetry, or two or one of them, and by combining them in every possible way, thirty-two different cases are obtained.

All the crystals which occur correspond to one of these cases, so that by the application of the principle of symmetry a complete system of all possible crystalline forms is obtained.

257. The Seven Systems of Crystals.—Into all these cases however, we cannot enter, but must content ourselves with the characterisation of seven of the larger groups.[1]

Owing to the necessity for brevity the chief characteristics of these groups cannot, it is stated, they cannot be described exactly. A less incomplete description will be found in Groth's *Physikalische Krystallographie* (Leipzig).

Crystals possessing the least symmetry (no element of symme
or a binary symmetry of rotation and reflection) are called *tricli*
The simplest form of this is the oblique angled parallelopiped (Fig. 8

Crystals with *one plane of symmetry* are called *monoclinic.*

Fig. 81.   Fig. 82.   Fig. 83.
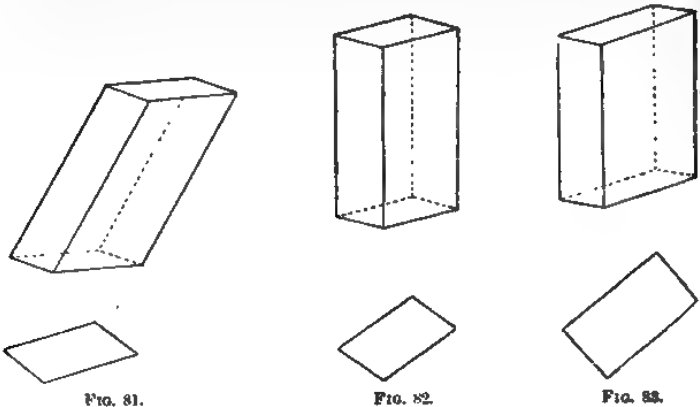
simplest form is the parallelopiped with four rectangular and t
oblique angled faces (Fig. 82).

Crystals with two planes of symmetry perpendicular[1] to one anot

Fig. 84.   Fig. 85.   Fig. 86.   Fig. 87.
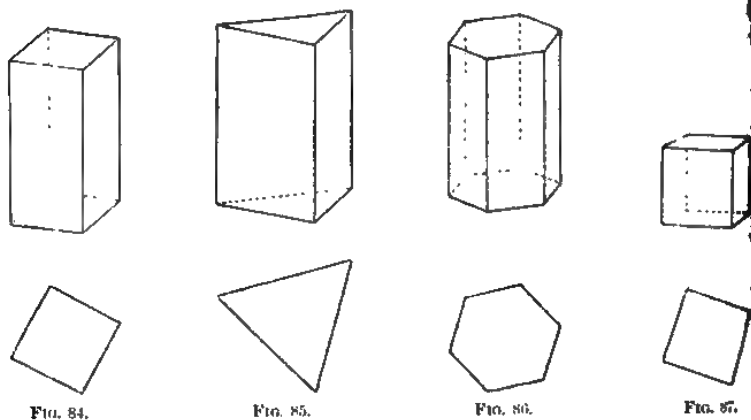
are called *rhombic.* Their simplest form is a rectangular parallelopip
(Fig. 83).

Crystals with a quaternary axis of symmetry are called *quadra*

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[1] When two planes of symmetry are not at right angles to one another, a third
of symmetry is required by the reflection of the one in the other, and by the refl
of this third, a fourth, etc. If, therefore, more than two planes of symmetry
in a straight line, are to be excluded, they must be perpendicular to one an

simplest form is a rectangular parallelopiped with quadratic base

Crystals with a ternary axis of symmetry are called *trigonal*. The simplest form is a three-sided right prism (Fig. 85).

Crystals with a senary axis of rotation are called *hexagonal*. The simplest form is the six-sided right prism (Fig. 86).

Crystals with three binary axes of symmetry perpendicular to one another and also *equivalent* are called *regular*. By equivalent is meant that the crystal always presents the same shape when it is turned so that its axes of symmetry assume positions previously occupied by other axes of symmetry. The simplest form of the regular crystals is a cube (Fig. 87).

Derived Forms.—Besides the simplest forms just mentioned, there are many others derivable from them geometrically, which obey the laws of symmetry valid for the particular kind of crystal.

The possibilities which arise are, however, so numerous that they cannot be treated here. We shall, however, state a law which makes their mutual connection clear.

Imagine a large number of small crystals of one of the simplest forms mentioned above, and all of the same size, to be given. By

arranging these in a regular
manner other forms can be
built up. From a number of
small cubes, for example, the
form shown in Fig. 88, which
is known as an octahedron,
can be built up. It is only
necessary to imagine new planes
put through the corners of the
cubes touching these corners,
or what amounts to the same
thing, one imagines the cubes to
be so small that the unevenness
caused by the re-entrant corners
can no longer be noticed.
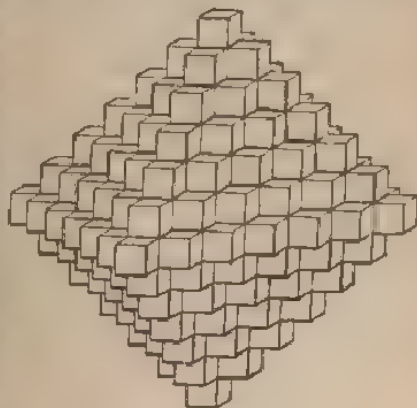
The law in question states
that every substance, occurring in different

Fig. 88

forms, of a substance, can be built up in the manner described from small crystals of the simplest form, the conditions of symmetry being at the same time observed.

The law stated here can be expressed mathematically in various ways. What we have said will be sufficient to show that the crystalline form of a given substance can be characterised by the statement of the simplest form.

The Other Properties of Crystals.—As has already been stated at p. 264, all the properties of crystals which can in any

way become dependent on the direction in space, have a regular orientation. The question arises, therefore, whether any connection exists between the external shape of the crystals and the orientation of the other properties.

The answer is that such a connection certainly exists. It can be stated thus: *The symmetry in the arrangement of the other properties is always contained in the symmetry relations of the external form.*

Let us take, as an example, a chemical phenomenon which readily occurs in the case of hydrated crystals, viz *efflorescence*. This consists in the water evaporating at different points of the crystal, a compound containing less water, which can be distinguished from the main portion by its different colour, remaining behind as a powder. If the efflorescence is allowed to take place with such precautions as to avoid the formation of detached spots, it can be established that the regions of efflorescence assume forms which have the same properties as regards symmetry as the crystal forms, and the position of which also corresponds to these forms.

If the crystal is *regular*, the efflorescence figure is always a *sphere*, for in regular crystals there are three planes of symmetry perpendicular to one another and equivalent. Of the shapes mentioned as occurring, the sphere and the ellipsoid, the sphere is the only one through which three equivalent perpendicular planes of symmetry can be laid.

The crystals of the *trigonal*, *quadratic*, and *hexagonal* systems have one axis of symmetry in which three, four, or six planes of symmetry lie. An ellipsoid which can be divided in this way must be a *uniaxial* one, *i.e.* an ellipsoid produced by the rotation of an ellipse about one of its axes. This axis of rotation must coincide with the axis of symmetry of the crystal, since it is only in this way that the ellipsoid can be divided by the corresponding planes of symmetry into three to six identical portions.

It is not possible, however, to distinguish tri-, tetra-, or hexagonal crystals by the difference of the ellipsoids of efflorescence. For a monoaxial ellipsoid may contain any number whatever of planes of symmetry laid through its axis of rotation. It makes no difference, therefore, whether there are three, four, or six.

Besides the monoaxial ellipsoid, there is the triaxial. It is produced by the rotation of an ellipse about one of its axes, the other axis being lengthened or shortened during the rotation, so that its ends (and at the same time also all other points of the ellipse) describe not circles but ellipses. Such a form has *three* planes of symmetry, which are determined by the axes of the generating ellipse, and are perpendicular to one another.

The same symmetry relations are also met with in the case of the *rhombic* crystals. It is to be expected, therefore, that the efflorescence forms of the rhombic crystals will be represented by triaxial ellipsoids.

...es of symmetry of which coincide with those of the crystalline
This conclusion is confirmed in every case by experience.
the case of monoclinic crystals only *one* plane of symmetry
Only one of the three planes of symmetry of the ellipsoid,
...re, can be determined by the crystalline form, and the two
...are indeterminate, *i.e.* they lie in a manner which is dependent
...nature of the crystal but not on its form.
...the case of triclinic crystals there is *no* plane of symmetry.
...ipsoid of efflorescence is, therefore, entirely independent of the

D. Generalisation.—What has just been stated for efflorescence.
...lso for many other properties of crystals, viz., for all those
...arrangement in the crystal can, in the most general case, be
...ated by a triaxial ellipsoid. Under this definition come the
...sion of light, of heat, of electricity, the changes of form by
... on all sides, and still other properties. The most important of
... the transmission of light, for the optical properties of crystals
...en subjected to a thorough scientific investigation, and are used
... identification of the crystalline system in those cases where the
...al shape gives no information or no complete information. It
...stated generally, that every optical phenomenon in a crystal is
... to the symmetry relations explained above, and that from the
...tion of the nature of the symmetry of any optical phenomenon
...r, a conclusion can be drawn as to the crystalline system,
...the limits stated.

C. *Sulphuretted Hydrogen*

The Compounds of Sulphur.—Sulphur is capable of forming
...nds with almost all elements, in some cases in very different
...ions. More especially, all *metals* form with sulphur com
... which have generally a similar composition to the corre
...ng oxygen compounds, and which are called *sulphides*. Many
...e occur abundantly in nature and form sources for obtaining
...als and also sulphur.
...her, sulphur forms a number of acids with hydrogen and
..., the chief of these being sulphuric acid. The salts of this
...e sulphates, also occur widely distributed in nature, and find a
...ed application in the arts and in medicine
...convince oneself of the power of sulphur to enter into com
...on, the following experiments may be performed. Heated in
... sulphur burns with a blue flame, forming an oxygen compound
...f choking smell, sulphur dioxide. A mixture of sulphur and
...wder in the proportion of 4 parts to 7, becomes incandescent
...g slightly heated, the *sulphur combining* with the iron to form
...slag-like mass of *iron sulphide*. If sulphur be heated to boiling

in a test tube and strips of thin copper-foil be introduced into
vapour, the copper becomes incandescent and combines with
sulphur, also forming a black compound.   Metallic mercury comb
with sulphur even at room temperature.   If 1 part of sulphur
rubbed together with 6 parts of mercury in a mortar, combination
takes place with formation of mercury sulphide of a deep black colour.
Likewise, silver combines with sulphur even at ordinary temperature;
silver coins and other objects of silver rapidly become black in
pocket in which sulphur matches have lain, the small quantities
sulphur present combining with the silver.

262. Sulphuretted Hydrogen.—Similarly to chlorine, bromine
and iodine, sulphur can combine with hydrogen to form an acid, which
is called hydrogen sulphide or sulphuretted hydrogen.   At ordinary
temperatures it is gaseous, but can be condensed by pressure and cold
to a liquid which boils, under atmospheric pressure, at – 64

The molar weight of sulphuretted hydrogen is 34 : it contains
parts of sulphur to 2 parts of hydrogen.   Since the combining weight
of sulphur is 32, the formula of sulphuretted hydrogen is H_2S.   Unlike
the halogen hydracids, sulphuretted hydrogen contains *two* combining
weights of hydrogen replaceable by metals, and in consequence of this,
there is an essential difference in the combining power of this acid.

263. Dibasic Acids.—If we consider what compounds can be
formed when the hydrogen of the sulphuretted hydrogen is replaced
by metals, *e.g.* sodium, we find there are *two* different salts concentrated
according as only *one* combining weight or *both* combining weights of
hydrogen are replaced by metal.   Expressed in formulæ, we should
expect the compounds, NaHS and Na_2S.   As a matter of fact, both
compounds are known.

To distinguish it from the acids which contain only one combining
weight of replaceable hydrogen, which can, therefore, react with only
one combining weight of a base to form a salt, and which are called
monobasic acids, sulphuretted hydrogen is called a *dibasic* acid.
Generally, a dibasic acid is one which contains in a mole, two com-
bining weights of replaceable hydrogen.

The salts of dibasic acids in which both hydrogens are replaced
by metals, are called *neutral* or *normal* salts.   Salts which contain only
one combining weight of metal along with one hydrogen, and which,
therefore, still contain the characteristic component of acids, hydrogen,
are called *acid* salts.

The former are also called *secondary* and the latter *primary*.
Further, they are designated by using the Greek numerals *mono*
and *di*-, which refer to the number of combining weights of metal
(not of hydrogen) present ; monosodium sulphide is the salt NaHS,
disodium sulphide, Na_2S.   Finally, compounds containing the group
HS are called *hydrosulphides*.   NaHS is sodium hydrosulphide.   All
these terms are in use side by side.

The Ions of Dibasic Acids—Whereas monobasic acids dissociate into ions in only one way, two different reactions are possible in the case of the dibasic acids, yielding two different kinds of anions. The dissociation occurs, in the first place, according to the equation

$$H_2A = H^. + HA',$$

where A is the divalent anion of the acid. That is to say, a monovalent anion HA' is formed along with hydrion. This process corresponds exactly to the ordinary electrolytic dissociation of the monobasic acids.

A new reaction, however, then occurs, viz.:—

$$HA' = H^. + A'',$$

the monovalent anion undergoing a further dissociation into hydrion and the divalent anion A''. The reaction

$$H_2A = 2H^. + A'',$$
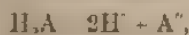
which might be regarded as that directly taking place, can be conceived of as the result of two processes occurring one after other.

The aqueous solutions of such acids, therefore, always contain two kinds of anions, and the different acids are distinguished by the extent to which the one or other process takes place.

The dissociation of a dibasic acid into its ions always begins with the first reaction. If the acid is not very strong, this process greatly predominates, and the second stage of the dissociation takes place only to a slight degree. In other words, such acids behave exactly like monobasic acids, dissociating into hydrion and a monovalent anion.

On the other hand, if the acid is very strong, the ion HA' further dissociates into H and A, and the solution will principally contain the divalent ion.

The solution of an acid salt of a *weak* dibasic acid, having the formula MHA, forms the ions M and HA', and as the latter possesses the power of dissociation only in a slight degree, only a small part of the ions HA dissociate further into A' and H. The acid salt, therefore, behaves approximately like a neutral salt and reacts feebly acid, neutral or (in consequence of hydrolysis, p. 250) alkaline in proportion as the acid decreases in strength.

If, however, we have a salt of a *strong* dibasic acid, the ions M and HA' are, it is true, first formed, but the latter undergoes further dissociation into the ions H and A''. The solution of such salt contains the ions A'', M, and H. Hydrion, therefore, is present in comparatively large amount, and the solution behaves principally like the solution of an acid.

An *example of the first case is afforded* by sulphuretted hydrogen,

even the primary salt of which undergoes hydrolysis and there[?]
reacts alkaline. We shall presently meet with an example of [?]
second case in sulphuric acid.

* On dissolving the neutral salt M_2A, the ions $2M'$ and A'' [?]
directly formed, and in the case of strong acids the matter rests th[?]
In the case, however, of a dibasic acid in which the second dissociat[?]
is only slight, a reverse action appears. Since the ion AH is mu[?]
more stable than the ion A'', there is a tendency for the former to [?]
produced at the expense of the latter. The hydrion which is pre[?]
in small amount through the dissociation of the water, is drawn [?]
to form this ion according to the equation $A'' + H = HA$. Hyd[?]
is thereby used up, and the corresponding amount of hydrox[?]
remains over. This is a process very similar to that of the hydr[?]
of the salt of weak monobasic acids (p. 250), the effect of which [?]
also that an excess of hydroxidion is finally present. The solut[?]
therefore, acquires an alkaline reaction; it turns red litmus pap[?]
blue, and phenolphthalein red.

265. **The Salts of Sulphuretted Hydrogen.** —The ab[?]
difference can be very clearly observed in the case of sulphuretted
hydrogen. The "acid" salts, e.g. NaHS, in aqueous solution, behav[?]
almost neutral to litmus; the normal salts, e.g. Na_2S, however, rea[?]
strongly alkaline. This is due to the fact that HS behaves as a[?]
extremely weak acid. In the solution of the sodium salt NaHS th[?]
ion present, $-HS$, is so slightly dissociated that the reaction of th[?]
hydrion, the reddening of litmus, is not visible. In the solution [?]
the normal salt, hydrolysis (*vide supra*) occurs to a large exten[?]
according to the equation

$$S'' + H_2O = HS' + OH'.$$
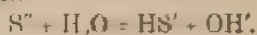
The hydroxidion formed is the cause of the turning blue of red litmu[?]
or, in general, of the alkaline reaction

* The relations described here are very frequently found, and var[?]
only with the relative strength of the dibasic acids with respect t[?]
their two hydrogen ions. More especially is hydrolysis of the [?]
salts of very frequent occurrence in the case of dibasic acids of me[?]
strength. Hence arises the contradiction that the salts, which [?]
account of both hydrogens present being replaced by metals, are [?]
neutral salts, do not react neutral but alkaline. It is preferably ther[?]
fore, to use the term *normal* salts, or one of the other names giv[?]
on p. 270.

266. **Preparation** —Sulphuretted hydrogen is obtained by the
decomposition of its salts, the metallic sulphides, by stronger acid[?]
Thus, it can be obtained from the two sodium salts of sulphuretted
hydrogen by means of hydrochloric acid, according to the equation[?]

$$Na_2S + 2HCl = 2NaCl + H_2S,$$
$$NaHS + HCl = NaCl + H_2S.$$
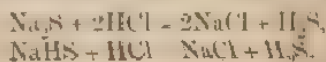
As can be seen from the second equation, the acid salt is the more economical for the preparation of sulphuretted hydrogen, since for the same amount of salt only half the amount of hydrochloric acid is required.

On account, however, of its cheapness, *iron* sulphide is generally used instead of sodium sulphide for the preparation of sulphuretted hydrogen. We have already got to know this substance as the product of the interaction between sulphur and iron (p. 269); it is also prepared on the large scale in a similar manner. Under the influence of hydrochloric acid the following reaction takes place :—

$$FeS + 2HCl = FeCl_2 + H_2S.$$
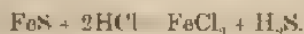
The iron sulphide consists of equal combining weights of iron and sulphur; the symbol Fe denotes iron. On comparing the formula of this compound with that of sulphuretted hydrogen, H_2S, it is seen that one combining weight of iron has taken the place of *two* combining weights of hydrogen. Such metals are called *divalent*, whereas metals which, like sodium, can replace only one combining weight of hydrogen, are called *monovalent*. Trivalent and polyvalent metals are also known.

Sulphuretted hydrogen is prepared and used in large quantities in the laboratory on account of its action on metallic salts, which will be presently mentioned. For its preparation on a comparatively small scale, the apparatus described on p. 87 can be used, iron sulphide, in large pieces, being introduced into the lower part and decomposed with hydrochloric or sulphuric acid. Where, however, larger quantities of sulphuretted hydrogen are regularly required, the apparatus shown in fig 89 will be found serviceable

This consists of three bottles with tubulures at the bottom, placed one above the other. From the top bottle a tube passes to the bottom of the middle one, and from the neck of this a tube, carrying a pinch cock, passes to the lowest bottle, which is filled with iron sulphide. The sulphuretted hydrogen is led away through a short tube, also fitted with a cock, which passes through the doubly-bored cork of the lowest bottle

If the top bottle be filled with dilute hydrochloric acid and two cocks opened, the acid first flows into the middle bottle, and as it passes in drops, by suitable regulation of the cock, to the sulphide in the lowest bottle The sulphuretted hydrogen is evolved, and can be led off through the second tube to be u

Fig. 89

T

ably small, vapour pressure, so that the law of
regarded as valid for all substances.   This is also
to be the case (p. 233).

The assumption, however, must remain fully
which is distributed undergoes no chemical ch
vents.   In such a case the law of distribution n
but the law of Henry also loses its validity (p
close connection between the two laws is seen

270   The Strength of Sulphuretted Hy
hydrogen is not a strong acid.   It can be
aqueous solution by boiling or by means of
which cannot be done in the case of the sol
acids, such as hydrochloric acid.   Its salts, a
by other acids, as is evident from the desc

The determination of the electrical co
tions of sulphuretted hydrogen yields ve
it may be concluded that only quite a sm
passed into ions, the greater portion b
sulphuretted hydrogen   When, therefor
come together in solution, they at one
of quite a small residue, to form undiss
and if the concentration of this is g
solubility under atmospheric pressure,
of bubbles.

As a matter of fact, in the ev
sulphide in solution and hydrochlori
be assumed :—

$$Na_2S + 2HCl$$
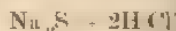
or, since on both sides the sodion

$$S'' + 2h$$

271. Theory of the Evolut
from Iron Sulphide.—How a
the gas from hydrochloric acid
generally regarded as *insoluble*
is *not* insoluble, although it
solubility, however, is sufficient
the solution along with diferim

$$S$$

takes place, more iron sulph
repeated so long as iron s
Only when the concentratio
and that of the diferrion
established, and the evolut

Hydrogen by Heat.

On being heated
ur and hydrogen
under the same
ding with a chemi

rogen. Sulphuretted
sulphur flame If the
walls of the cylinder
ur. This is due to the
drogen unites much more
does. Therefore, if there
cylinder, only the hydrogen
this case also, the sulphur is
division

drogen. That sulphuretted
sent by the experiment just
be proved by converting this

mercury oxide, is heated in
The following reaction then

$HgS + H_2O$
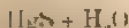
nd water are formed. The latter
receiver and identified by its pro-

phuretted hydrogen can be set free by
divided copper is heated in a current
flowing reaction takes place

$Cu \quad CuS + H_2$.
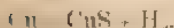
hydrogen are produced.
using sulphuretted hydrogen with forma-
ngs also to the noble metals, especially to
this reason, silver objects become black in
ng sulphuretted hydrogen To
ng of silver spoons which come in
dishes.
tes.—When a solution of sodium
phur, the latter dissolves and the l
By evaporation of the soluti
Na_2S can be obtained in the cryst

when diferrion and disulphidion come together in solution, that compound being formed according to the equation

$$Fe + S = FeS$$

This occurs, for example, when a solution of sodium sulphide is mixed with one of ferrous chloride

$$Na_2S' + Fe''Cl_2 = FeS + 2NaCl'.$$
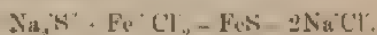
For this reason a black precipitate of iron sulphide is obtained under these conditions.

Those difficultly soluble metallic sulphides which are not precipitated in acid solution by sulphuretted hydrogen, can be precipitated from a neutral solution by sodium sulphide, or similar readily soluble sulphides. This behaviour is also made use of in analytical chemistry.

273. Sulphuretted Hydrogen as a Reducing Agent. exposed to the air, a solution of aqueous sulphuretted hydrogen soon becomes turbid and deposits a white precipitate. The liquid which remains is pure water. The process consists in the oxidation of the sulphuretted hydrogen by the oxygen of the air

$$2H_2S + O_2 = 2H_2O + 2S.$$

The sulphur separates out in a state of very fine division, and has, therefore, the white colour of milk of sulphur (p. 259).

By reason of this power of combining with oxygen, sulphuretted hydrogen acts as a reducing agent, and it is occasionally used for the purpose of removing oxygen. Similarly, hydrogen compounds can be prepared with the help of sulphuretted hydrogen.

274. Preparation of Hydrogen Iodide. If, for example, sulphuretted hydrogen be passed into water in presence of iodine, the following reaction takes place
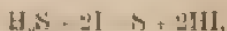
$$H_2S + 2I = S + 2HI,$$
or, expressed as ions: $$S' + 2I = S + 2I'.$$

That is, from sulphuretted hydrogen and iodine, hydrogen iodide and sulphur are formed. In this way an *aqueous solution* of hydrogen iodide can be easily prepared.

On the other hand, *gaseous* hydrogen iodide, on gently heating, acts on sulphur with formation of iodine and sulphuretted hydrogen gas. The cause of this difference lies in the fact that in the former case the hydrogen iodide dissolves in water and passes into its ions. The ions of hydriodic acid are much more stable than hydrogen iodide itself, and are therefore formed under the above conditions. In the second case, no water is present, and the greater stability of the sulphuretted hydrogen compared with the undissociated hydrogen iodide, causes in *that case the reversal of the process.*

275 Decomposition of Sulphuretted Hydrogen by Heat.
Sulphuretted hydrogen itself is also not very stable. On being heated in a red-hot tube, it partially decomposes into sulphur and hydrogen. On the other hand, sulphuretted hydrogen is formed under the same conditions from its elements, so that we are here dealing with a chemical equilibrium according to the equation

$$H_2 + S \rightleftarrows H_2S$$
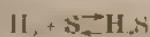
276 Combustion of Sulphuretted Hydrogen. Sulphuretted hydrogen readily burns in the air with a blue sulphur flame. If the gas contained in a cylinder be ignited, the walls of the cylinder become covered with a white coating of sulphur. This is due to the fact that the hydrogen of the sulphuretted hydrogen unites much more readily with the oxygen than the sulphur does. Therefore, if there is a scarcity of air, as in the interior of the cylinder, only the hydrogen burns and the sulphur separates out. In this case also, the sulphur is coloured white by reason of its state of fine division.

277 Analysis of Sulphuretted Hydrogen. That sulphuretted hydrogen contains sulphur, is made evident by the experiment just described; the presence of hydrogen can be proved by converting this into water.

For this purpose a metallic oxide, e.g. mercury oxide, is heated in a current of dry sulphuretted hydrogen. The following reaction then takes place

$$HgO + H_2S = HgS + H_2O$$

that is to say, mercury sulphide and water are formed. The latter can be easily collected in a cold receiver and identified by its properties.

Further, the hydrogen of sulphuretted hydrogen can be set free by metals. For example, if finely divided copper is heated in a current of sulphuretted hydrogen, the following reaction takes place

$$H_2S + Cu = CuS + H_2$$

that is, copper sulphide and hydrogen are produced.

This property of decomposing sulphuretted hydrogen with formation of metallic sulphides extends also to the noble metals, especially to mercury and to silver. For this reason, silver objects become black in contact with air containing sulphuretted hydrogen. To the same cause is due the blackening of silver spoons which come into contact with albumen-containing substances.

278 Polysulphides. When a solution of sodium sulphide is boiled together with sulphur, the latter dissolves and the liquid becomes yellow in colour. On evaporation of the solution, compounds of sodium Na_2S can be obtained in the crystalline state. The

solutions themselves behave quite similarly to those of sodium sulphide; they conduct electricity, and are, therefore, to be regarded as salt solutions. The ions are, on the one hand, sodion Na^{+}, and, on the other hand, S_{2}'' to S'', or HS_{2}' to HS_{5}'.

The relations are similar to those in the case of iodine, where the ion I' can pass into the brown ion I_{3}' by taking up two further combining weights of iodine (p. 238).

Of the polysulphidions only S_{4}'' and S_{5}'' have been characterised with any degree of exactness; the lower ones behave like mixtures of S and S_{4}'.

279. Hydrogen Persulphide. The above solutions behave differently when acted on by acids, according as the acid is added gradually to the solution, or the solution poured into excess of acid. In the first case, sulphuretted hydrogen is evolved and the excess of sulphur separates out as milk of sulphur; this is the usual way of preparing milk of sulphur, sodium sulphide, however, being replaced by calcium sulphide. The reaction takes place according to the equation

$$Na_{2}S_{5} + 2HCl = 2NaCl + H_{2}S + 4S,$$
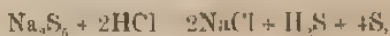
when the pentasulphide is used, and in a corresponding manner with the other sulphides.

If, however, the concentrated solution of the sulphide be added to excess of hydrochloric acid, no sulphuretted hydrogen escapes, but only drops separate out and unite to a yellow liquid. This has the composition $H_{2}S_{n}$, where n lies between 2 and 5. It is called hydrogen persulphide, and may be regarded as a mixture of the acids $H_{2}S$ and $H_{2}S_{5}$, in which varying amounts of hydrogen sulphide are dissolved.

The liquid is very unstable, readily undergoing spontaneous decomposition into sulphur and sulphuretted hydrogen. It exhibits, in this respect, some resemblance to hydrogen peroxide, for its decomposition is promoted by such substances as mechanically facilitate an evolution of gas. Differences are found only in so far as the hydrogen persulphide is but sparingly soluble in water.

* 280. Thermochemical Data.—Sulphuretted hydrogen is formed from solid rhombic sulphur with development of 11 kj; in solution in water further 19 kj are developed, so that the heat of formation of dissolved sulphuretted hydrogen is 30 kj.

In the formation of hydrogen persulphide, an absorption of heat equal to 22 kj accompanies the taking up of the first atom of sulphur. In this respect, therefore, there is a similarity to hydrogen peroxide. The rest of the sulphur is dissolved without appreciable heat effect.

The heat of neutralisation amounts, for the first equivalent, to 32 kj, for the second, to zero. From this it likewise follows that the reaction consists essentially in the formation of the salt $NaHS$, or of the ions $Na + HS'$, and that sodium sulphide in dilute solution reacts

...tion $Na_2S + H_2O \quad 2Na' + HS'$
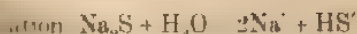
... value that the formation of the
... tted hydrogen, gives 32 – 57
... strong absorption of heat, which
... in the case of hydrofluoric acid.

H.S aq.   Na'HS' aq. + 32 kj
OH + H' H_2O + 57 kj
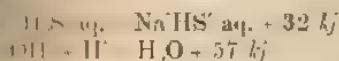
... lower from the upper and omission of the

S aq   H HS' aq.   25 kj.
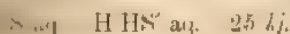
... *Dioxide and Sulphurous Acid*

...ition. – In the combustion of sulphur in air or
...med which causes the well-known pungent smell of
... and is a compound of sulphur

...mbustion is carried out in an
... in the apparatus, Fig. 90),
... that the volume of the gas is not
...erent from that of the oxygen.[1]
... oxygen is O_2, the compound which is
... an equal volume must also contain
... ...ing weights of oxygen.
... ...lar weight of the gas has been found
... 64 or somewhat over this, according
... ...sure and temperature. It contains,
... along with $2 \times 16 = 32$ parts of

Fig. 90

... 32 parts or one combining weight of sulphur, and its formula

2. **Physical Properties.** —Sulphur dioxide is a gas which,
... small pressures, exhibits deviations from Boyle's law, in the
... that as the pressure increases the volume diminishes more than
...tionally to the pressure. Further, it can be liquefied by
... pressure and cold. At atmospheric pressure, the temperature
...eezing mixture of ice and salt is sufficient; if sulphur dioxide
... into a glass vessel surrounded by this mixture, it condenses
...ery mobile liquid as clear as water. In the following table is
... the relation between pressure and temperature :-

... rule, the volume is somewhat smaller, because along with the compound is
... also formed some SO_3, which combines with traces of moisture present, and is a
...latile compound

Temperature.	Pressure	Temperature	Pressure.
30	0.49 atm.	+ 5	1.87 atm.
25	0.49 ,,	10	2.26 ,,
20°	0.63 ,,	15°	2.72 ,,
15	0.80 ,	20	4.24
10	1.00 ,	25	3.84 ,,
5	1.25 ,,	30	4.52 ,,
0	1.53 ,,	10	0.15

As can be seen, the boiling point at atmospheric pressure is − 10
The critical magnitudes are : pressure 79 atm., temperature 157

Liquid sulphur dioxide is now placed on the market in metal
cylinders, similarly to liquid chlorine   In cases where large quanti
ties of the substance are required, the use of such cylinders is very
convenient.

283 Behaviour towards Water.   Sulphur dioxide dissolves
fairly abundantly in water   At higher temperatures the solubility
follows to some extent the law of Henry.   At room temperature one
volume of water dissolves about 50 volumes of sulphur dioxide

The aqueous solution smells strongly of the gas, which can be
entirely expelled by boiling.   Towards litmus, the solution shows
the reaction of an acid ; it therefore contains hydrion.   Since sulphur
dioxide does not contain any hydrogen, the acid must have been
produced by the union of it with water, and therefore have the
formula $SO_2 + nH_2O$ The value of n cannot be ascertained by an
analysis of the liquid, since this contains excess of water.   If, how
ever, the liquid be neutralised with caustic soda and the sodium salt
of the acid present prepared by evaporation, this is found to have
the composition Na_2SO_3.

From this it is to be concluded that the acid has the composi
tion H_2SO_3.

284. Sulphurous Acid.   This acid, known not in the pure con
dition but only in solution, is called *sulphurous acid.*   Sulphur dioxide
is sometimes designated by this name, but that is incorrect.   Rather,
it must be called sulphurous acid anhydride, because it is formed
from sulphurous acid by loss of water.   As can be guessed from the
formula, and as is found by analysis of the salts, sulphurous acid is
a dibasic acid, and can form normal salts of the formula M_2SO_3 and
acid salts $MHSO_3$, where M represents a combining weight of a
monovalent metal.

285. Dissociation of Sulphurous Acid.—In the sense of the
considerations set forth on p. 244, sulphurous acid is a comparatively
weak acid, the second hydrogen of which shows very little tendency
to pass into the ionic state.   This is evident from the fact that the
acid cannot be titrated with caustic soda and litmus   Even before the
equivalent amount of base has been added, the colour changes slowly
and continuously from red, through violet, to blue, without it being
possible to distinguish a sharp transition.   Accordingly, the aqueous

solution of the normal sodium salt, which has been purified by repeated recrystallisation, also exhibits an alkaline reaction. This arises through the action of the water on the ions of the salt. According to the equation

$$Na_2SO_3 + H_2O \quad Na'HSO_3' + Na'OH ,$$

the ion of the acid sulphites HSO_3 is formed at the expense of the water, hydroxidion being thereby also produced, which causes the characteristic blue coloration of litmus. This reaction, however, takes place to a less extent than in the case of sulphuretted hydrogen (p. 271).

286. Bleaching Action. Sulphurous acid and its salts possess some properties which are of importance technically. Sulphurous acid bleaches various organic colouring substances, and is therefore used for the decoloration of silk and wool. These substances cannot be bleached with chlorine, because they thereby become hard and brittle.

To carry out the process of bleaching, the substances are hung up in a moist condition in chambers which can be closed, and in these the sulphur dioxide required is generated by the combustion of sulphur When after some time the bleaching has taken place, the substances must be carefully washed in order to remove the transformation products of the colouring substances and the excess of sulphurous acid

* This property can be clearly demonstrated by placing a number of coloured flowers near burning sulphur, and covering the whole with a glass bell jar. In a short time all the flowers become white

* The colour, however, is not completely destroyed, as in the case of chlorine, but can be restored This takes place, to a certain extent, spontaneously, on standing some time in the air ; more quickly by moistening the bleached blossoms with dilute sulphuric acid. Under these conditions blue colours which are turned red by acids do not, of course, appear again ; in their place red appears

287. Physiological Action.—Sulphurous acid has, further, a powerful action on vegetable organisms, from the highest orders down to the moulds and similar forms of life This shows itself in an undesirable manner in the neighbourhood of foundries and chemical works in which sulphur dioxide is generated and in part diffused through the air, in the fact that vegetable growth more or less completely dies out. Even the sulphur contained in coal produces similar effects in towns This important property of sulphurous acid finds useful application in the "curing" of wine and beer for the purpose of keeping away mould and other organisms, which would have a detrimental action on these liquids This is the purpose of the process of *sulphuring* wine casks, i.e. of burning sulphur in the interior of the which has been in vogue from remote times. For similar pur large quantities of sulphurous acid salts are used in breweries.

Temperature.	Pressure
-30°	0·39 atm.
25	0·49 ..
-20°	0·63 ..
-15°	0·80 ..
10°	1·00 .
-5°	1·25 ..
0°	1·53

As can be seen, the boiling
The critical magnitudes are : :

Liquid sulphur dioxide
cylinders, similarly to liquid
ties of the substance are n
convenient.

283. **Behaviour** tow
fairly abundantly in wa
follows to some extent th.
volume of water dissolv

The aqueous soluti
entirely expelled by heal
the reaction of an acid
dioxide does not com
produced by the un
formula $SO_2 + nH_2O$
analysis of the liquo.
over, the liquid be
of the acid present
the composition N

From this it
tion H_2SO_3.

284. **Sulp**
dition but only
is sometimes de
it must be con
from sulphur
formula, and .
a dibasic acid,
acid salts M
monovalent n

285. **Di**
consideration
weak acid, th
to pass int
acid cannot
equivalent
and com
possible.

... ..e of sulphur d
... ..s is carried ou
... ..s of the oxyg
... . ..her employed
... ..n aqueous solu
... ..r 10 per cent
... ..ed solution o
... . sulphur dioxic
... ..lly, and is em
... ..r.c is also the m
... ..e for laboratory p
... ..centrated sulph
... ..i delivery tube,
... ..e dropping funnel
... ..t the same time
... ..o water, which r

... ..phurous acid readily a
... ..ich has the composit
... ..s acid is a *reducing a*
... ..cessary for this transf
... can also be removed
... hydrogen of entering
... ..en acts not by withd
... ..xample of this last pro
... .n iodine, which takes

... .. - $H_2O = H_2SO_4 + 2HI$.

... ..into hydriodic acid. Si
... ..detected by means of s
... ..ed for the volumetric de
... ..e of sulphurous acid with
... ..uch employed, has now b
... ..ent methods. The inconve
... ..at the composition of th
... ..ly undergoing change, ow.
... ..e by the oxygen of the air.
... ..act on iodine in the sam
... ..but they have the secon
... ..e oxygen of the air can, howe
... ..ding to the solution a sma
... ..or similar substances. So sm
... ..e weight of the solution is suf
... ..itself undergoes no change ;
... ..ed as a catalytic one.

...ous **Acid**   From the hot, concentrated solu-
...t the alkali metals, salts crystallise out which
...position of acid salts, because they contain no
...um salt, more especially, forms very readily,
...the composition represented by the formula
...g this formula with that of the acid sulphites,
...h t the salt has been formed from this, with the
...t water—

$$2KHSO_3 \quad K_2S_2O_5 + H_2O.$$

...mon which is combined with potassium is therefore
...corresponding acid must, accordingly, have the formula
...be looked upon as a compound of sulphurous acid
...xide—

$$H_2SO_3 + SO_2 \quad H_2S_2O_5$$

...ver, it be attempted to prepare this acid from the
...salt, only the ordinary sulphurous acid is obtained   The
...therefore, passes at the moment of its liberation into
...acid or, what is perhaps more correct, the sulphurous
...contains small amounts of the acid $H_2S_2O_5$ along with the
...acid ; the different forms, however, pass so quickly into
...ther that they cannot be investigated individually.

...acid $H_2S_2O_5$ is called *pyrosulphurous acid*, and its salts are
...pyrosulphites.   The name is due to the fact that a similar
...re of phosphoric acid has been obtained by heating that acid

Thermochemical Relations.   The combustion of sulphur
...ous dioxide develops 297 k_j, the solution of the latter in
...further 3.? l_j, so that the heat of formation of the aqueous
...29.? ?   When one equivalent of caustic soda is added to the
...n, 67 k_j are developed : a second equivalent yields further
...From this it follows that the formation of the ions H and
...from the undissociated acid, H_2SO_3, takes place with a
...ment of heat of more than 10 k_j, since the acid is already
...dissociated, the whole amount of heat does not show itself
...ond dissociation, $HSO_3' H + SO_3''$, appears to take place
...t any considerable heat effect, since the heat of neutralisation
...very near to the normal 57 k_j

E. *Sulphur Trioxide and Sulphuric Acid*

Sulphur Trioxide   Although sulphur dioxide is not the
...compound of oxygen with sulphur, it is essentially the only one
...produced in the direct interaction, *i.e.* in combustion, even
...xygen is present in great abundance.   A higher oxide of

...n of sulphur dioxide and ...
... is carried out by burning ...
... ...ns of the oxygen in the a...
... either employed as such or ...
... an aqueous solution saturated
... only 10 per cent of sulphurous
... ...rated solution of acid soum...
... of sulphur dioxide on sodium
... ...rcially, and is employed for the
... ...ion is also the most convenient
... ...e for laboratory purposes. Fo...
... concentrated sulphuric acid in a ...
... and delivery tube, and to allow
... the dropping funnel. The sodium
... at the same time the sulphurous
... into water, which remains behind

... ...phurous acid readily absorbs oxygen
... which has the composition H_2SO_4, an...
... ...us acid is a *reducing agent*, because ...
... ...essary for this transformation from
... ...n can also be removed from water it
... ...hydrogen of entering into another
... then acts not by withdrawing oxygen
... ...xample of this last process is afforded
... ...on iodine, which takes place according

$$... + H_2O \quad H_2SO_4 + 2HI.$$
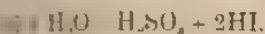
... into hydriodic acid. Since very small
... ...e detected by means of starch (p. 235)
... ...sed for the volumetric determination of
... ...of sulphurous acid with iodine. The
... much employed, has now been abandoned
... ...ent methods. The inconvenience of the
... that the composition of the solutions is
... ...ly undergoing change, owing to escape
... ...by the oxygen of the air. Solutions of
... act on iodine in the same way, do not
... but they have the second. The spo...
... oxygen of the air can, however, be almost
... ...ing to the solution a small quantity of
... or similar substances. So small a quantity
... ...e weight of the solution is sufficient for th...
... itself undergoes no change; the action has
... ...ted as a catalytic one.

290. Pyrosulphurous Acid. From the hot, concentrated solutions of the acid sulphites of the alkali metals, salts crystallise out which do not have the composition of acid salts, because they contain no hydrogen. The potassium salt, more especially, forms very readily, and is found to have the composition represented by the formula $K_2S_2O_5$. On comparing this formula with that of the acid sulphites, $KHSO_3$, it is seen that the salt has been formed from this, with the loss of the elements of water

$$2KHSO_3 = K_2S_2O_5 + H_2O$$
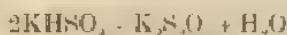
The divalent anion which is combined with potassium is therefore S_2O_5'', and the corresponding acid must, accordingly, have the formula $H_2S_2O_5$. It can be looked upon as a compound of sulphurous acid and sulphur dioxide—

$$H_2SO_3 + SO_2 = H_2S_2O_5$$
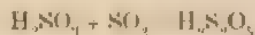
If, however, it be attempted to prepare this acid from the potassium salt, only the ordinary sulphurous acid is obtained. The new acid, therefore, passes at the moment of its liberation into sulphurous acid, or, what is perhaps more correct, the sulphurous acid also contains small amounts of the acid $H_2S_2O_5$ along with the ordinary acid; the different forms, however, pass so quickly into one another that they cannot be investigated individually.

The acid $H_2S_2O_5$ is called *pyrosulphurous acid*, and its salts are called pyrosulphites. The name is due to the fact that a similar derivative of phosphoric acid has been obtained by heating that acid.

291. Thermochemical Relations.—The combustion of sulphur to gaseous dioxide develops 297 kj, the solution of the latter in water, further 32 kj, so that the heat of formation of the aqueous acid is 329 kj. When one equivalent of caustic soda is added to the solution, 67 kj are developed; a second equivalent yields further 55 kj. From this it follows that the formation of the ions H and HSO_3 from the undissociated acid, H_2SO_3, takes place with a development of heat of more than 10 kj; since the acid is already slightly dissociated, the whole amount of heat does not show itself. The second dissociation, $HSO_3 = H + SO_3$, appears to take place without any considerable heat effect, since the heat of neutralisation 55 kj is very near to the normal 57 kj.

E. Sulphur Trioxide and Sulphuric Acid

292. Sulphur Trioxide.—Although sulphur dioxide is not the highest compound of oxygen with sulphur, it is essentially the only one which is produced in the direct interaction, i.e. in combustion, even when oxygen is present in great abundance. A higher oxide —

indeed, that it cannot be made use of for manufacturing purposes. For this reason, the sulphuric acid was formerly prepared in another way, viz., by strongly heating iron vitriol or sulphate of iron. This process is, chemically, not very simple, and the details of it will be given under iron. It has, at the present day, only an historical importance, since it is no longer used.

The method still chiefly employed at the present time (cf. p. 286) depends on the oxidation of sulphur dioxide or sulphurous acid, but this is accelerated by a particular expedient to such an extent that it has become a productive manufacturing method.

The method was developed from experiments made to replace the oxygen of the air by more quickly acting oxidising agents. Sulphur was burned with the addition of potassium nitrate or saltpetre. This substance has the formula KNO_3, it contains, therefore, a large amount of oxygen, with which it readily parts. In these experiments it was found that much more sulphuric acid was produced than could have been formed from the oxygen of the saltpetre. The cause of this was found to be that the oxidation of the sulphurous acid by the oxygen of the air takes place much more quickly in the presence of the gaseous oxygen compounds of nitrogen which are produced under the above conditions than when it is alone.

297. Manufacturing Process. — The above mentioned process then amounted to this : Sulphur dioxide was formed by the combustion of sulphur, and the gas was mixed with air and water vapour in the amount necessary for the formation of sulphuric acid, the production of which was sufficiently accelerated by the addition of oxides of nitrogen. The various stages through which the process has passed cannot be described here ; it will be sufficient to give a description of the arrangement of a present-day sulphuric acid manufactory. The sulphur dioxide is, at present, generated only to a small extent from sulphur itself ; for its formation the sulphur compounds of iron are chiefly used. These are burned in suitable furnaces, forming iron oxide, which remains behind, and sulphur dioxide, which escapes. Large quantities of sulphuric acid are also formed from other ores containing sulphur, which, for the purpose of obtaining the metals in them, are "roasted," i.e. heated with access of air. The sulphur passes into sulphur dioxide, and the metals form oxides.

The hot mixture of sulphur dioxide and air is first of all led into an empty chamber, where the small, solid particles carried over with the gas, "flue-dust," are deposited.

The gases then enter at the foot of a tower (the Glover tower) filled with acid-resisting stones, and are met by a counter-stream of crude, dilute sulphuric acid, such as is formed in this process. By this arrangement the hot gases are cooled by causing the evaporation of the water contained in the dilute sulphuric acid ; the acid is thereby concentrated. At the same time, the acid is freed from the oxides

nitrogen which it contains (*vide infra*), and these are again brought
into the process. In this way, not only is a loss of these com-
paratively valuable substances avoided, but the sulphuric acid is at
the same time freed from an impurity which would be very detri-
mental in its further treatment and application.

From the tower, the gases pass into several large chambers lined
with lead plates (Lead is attacked by sulphuric acid to a
comparatively slight extent.) Into these chambers, steam and oxides
of nitrogen are also introduced; oxidation to sulphuric acid occurs,
which falls as a fine rain to the bottom of the chamber.

From the last chamber there escapes not only the nitrogen of the
atmospheric air, but also the oxides of nitrogen present, so far as they
have not been absorbed by the dilute acid formed in the chambers,
in the chamber acid. In order that these oxides may not be lost,
they are led through a second tower (the Gay-Lussac tower) in which
concentrated sulphuric acid is trickling in an opposite direction. The
acid readily dissolves large quantities of the oxides of nitrogen, and
retains this valuable material. The atmospheric nitrogen passes
up a large chimney, which maintains the draught through the whole
series of apparatus. The concentrated sulphuric acid charged with
oxides of nitrogen is introduced into the first tower, where the
oxides of nitrogen are given off.

Action of the Oxides of Nitrogen.—As to the cause of the
acceleration of the sulphuric acid formation by the oxides of nitrogen,
a theory has been in existence for a hundred years. According to
it the cause lies in the alternate reduction of the oxides by the
sulphur dioxide and their re-oxidation by the oxygen of the air.
The details of this theory cannot be discussed till the oxides of
nitrogen are treated. Since the oxides of nitrogen are found at the
beginning and the end of the process in the same condition, and are
not used up, we must at this point be satisfied with designating the
accelerating action as a catalytic one.

Concentration of the Acid. The acid obtained by this
method contains about 65 per cent of acid and 35 per cent of water.
This amount of water, in the form of steam, must be introduced into
the chamber in order that the formation of sulphuric acid shall
take place quickly and regularly. For most of the applications of
sulphuric acid, however, this water must be removed.

This is effected in the first place in flat lead pans which are
heated from above. When the sulphuric acid attains a concentration
of 80 per cent, it begins to attack the lead. It is then evaporated
further in flat platinum retorts. At first, almost pure water passes
off, but when the acid has reached a concentration of 98·5 per cent,
the vapour has nearly the same composition as the liquid, and further
concentration becomes impossible. Before the acid has reached this
point, it is run into carboys, in which it is transported.

U

303. The Ions of Sulphuric Acid.—Being a dibasic acid, sulphuric acid can form two kinds of anions, viz. the monovalent HSO_4' and the divalent SO_4''. Concentrated solutions of the acid chiefly contain the former; the greater the dilution, the more does this dissociate into the divalent ion and hydrion. Like almost all the ions hitherto mentioned, both these ions are colourless and possess no conspicuous properties.

304. Applications of Sulphuric Acid.—In the laboratory, and still more in the arts, sulphuric acid is a substance of immense importance and manifold application. Its importance for the chemical industry has been justly compared with that of iron for the engineering industry. The manifold application of sulphuric acid depends on the fact that it can be used in two ways for obtaining other acids from their salts. Since it is, as a rule, only the *salts* of the various acids that are got directly, and from these the free acids must then be obtained, an acid suitable for this object finds a very varied application.

The use of sulphuric acid for this purpose depends on the combination of several circumstances. Apart from its cheapness, the fact that it is a *strong* acid, i.e. one largely dissociated into ions, and has a *high boiling point*, is the determining factor.

Certainly, on making a comparison, it is found that in equivalent solutions, i.e. solutions containing equal amounts of hydrogen, hydrochloric acid is a better conductor than sulphuric acid, and that the former, therefore, is more dissociated. However, the somewhat smaller degree of dissociation of sulphuric acid (cf p. 247) is more than compensated for by its small volatility. Thus, hydrochloric acid is prepared from sodium chloride by means of sulphuric acid according to the equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The possibility of generating the stronger acid from its salts by means of the weaker, depends on the difference of the volatility of the two acids. When sulphuric acid acts on sodium chloride, only a small quantity of hydrochloric acid is at first formed, and the reaction would stop, i.e. a chemical equilibrium would be established, if all the substances remained together. Even on gentle heating, however, the hydrochloric acid passes off in the gaseous state. The equilibrium is thereby disturbed, fresh hydrochloric acid must be formed, and therefore, fresh sodium chloride be decomposed. If this hydrochloric acid be also removed, the process goes on until, finally, all the sodium chloride is decomposed or all the sulphuric acid is used up (cf p. 208).

In the decomposition of sodium chloride by sulphuric acid, and in similar processes, two stages can be clearly distinguished. The first half of the decomposition always takes place much more easily, i.e. at a lower temperature than the second. This depends on the differ-

...re of sulphuric acid. The process is separable into two stages, ...esented by the following equations : —

$$H_2SO_4 + NaCl = NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$
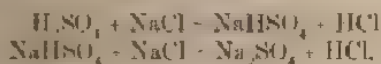
As in the case of all polybasic acids, the one combining weight of ...rogen splits off first and most readily ; the splitting off of the ...d occurs with much greater difficulty. For this reason, even when ...ombining weights of sodium chloride are present, there is, at ...rst, the acid sodium sulphate formed, according to the first ...tion, and one combining weight of sodium chloride remains. Not ...l this reaction is essentially over, and a higher temperature is ...ied, does the second process, the decomposition of the sodium ...de by the acid sodium sulphate, take place, with formation of the ...al sulphate.

Sulphuric acid can be used also in a second way for the prepara... of free acids from their salts. With some metals, especially ...m, Ba, and lead (Pb), it can form very difficultly soluble salts. ...fore, if aqueous solutions of the barium or lead salt of the acid ...estion be mixed with sulphuric acid, barium or lead sulphate is ...ed and separates out in the solid state, while the acid remains ...tion. In this way, for example, chloric acid, $HClO_3$, is obtained ...Pb.

Analytical Test. — This same circumstance, the *slight* ...y of *barium sulphate*, is employed for the detection and esti...on of sulphuric acid and its salts ; in general, of the ion SO_4'' ...ever barium, Ba", comes together with the ion SO_4'', the pre...te of barium sulphate $(BaSO_4)$ separates out. Since sulphuric ...s a fairly strong acid, the small solubility of barium sulphate is ...increased to any considerable extent by the presence of free ...p. 276. The reaction, therefore, is also given in *acid* solutions. ...s there any other substance by means of which barium sulphate ...rendered appreciably soluble in aqueous liquids. This reaction, ...fore, is a very *certain* criterion for the presence of SO_4'' ion, and ...error can arise only from the fact that selenic acid (*vide infra*), ...h is very similar to sulphuric acid, yields a similar, difficultly ...ble precipitate with barium salts. When we come to selenic acid, ...ever, we shall show how such an error can be excluded.

The question may be asked, if the two different ions, HSO_4' and ...do not, in conformity with the difference of their composition, ...different properties and characteristics. As to the former, there ...doubt ; but the detection of these differences is not easy, since ...presupposes a knowledge of the proportions of both ions in a given ...tion. Although this problem is not insoluble, still it is so com...ted that it cannot be discussed here.

On the other hand, for the detection and the estimation of sul-

phuric acid by barium compounds, it is a matter of indifference in what proportions the ions HSO_4' and SO_4'' are present in a solution. By precipitation as barium sulphate, certainly, only SO_4 ion is at first removed; so soon, however, as this takes place, a fresh amount is formed from HSO_4 ion, in accordance with the equation $HSO_4' =$ $H^{\cdot} + SO_4''$. This is also precipitated, and so on until practically all the sulphanion has been precipitated. Only when the concentration of the hydrion is very great, that is, when the solution is very acid, does a measurable quantity of HSO_4-ion remain undissociated, and is not precipitated. Hence the rule that the precipitation of barium sulphate must not be carried out in a too acid solution.

306. Decomposition of Sulphuric Acid.—Sulphuric acid is a fairly stable substance. It undergoes oxidation to a higher stage only under quite special conditions by means of the electric current. Reduction takes place more readily, and use is sometimes made of such processes for the preparation of sulphur dioxide. Such reduction occurs, for example, on heating sulphuric acid with copper.

Copper is a divalent metal, the sulphate of which has the formula $CuSO_4$. On heating copper with sulphuric acid, the usual displacement of hydrogen by metal would first take place—

$$Cu + H_2SO_4 = CuSO_4 + H_2.$$

The hydrogen, however, is not evolved, but is oxidised at the expense of the oxygen of a second mole of sulphuric acid; this is reduced to sulphurous acid, which immediately decomposes into sulphur dioxide and water. In formulæ,

$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$

The two equations can be combined into one, and we obtain

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$
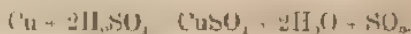
Mercury and silver behave similarly to copper. In the case of zinc the reduction goes still further, sulphuretted hydrogen being formed under certain circumstances

$$5H_2SO_4 + 4Zn = 4ZnSO_4 + 4H_2O + H_2S.$$
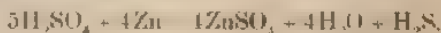
This reduction occurs only when the solutions are fairly concentrated. Dilute sulphuric acid reacts with zinc, with formation of hydrogen—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
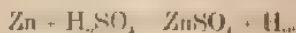
307. Pyrosulphuric Acid.—The compound of sulphuric acid with trioxide, $H_2S_2O_7$, mentioned on p. 287, is a special acid, to which the *name of pyrosulphuric acid has been given. For the compound of

exists itself, but the corresponding salts can be prepared, e.g. the salt $Na_2S_2O_7$. The salts are obtained by heating the acid salts, e.g.

$$2HNaSO_4 = Na_2S_2O_7 + H_2O.$$
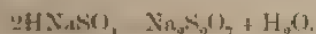
and more strongly, the salts lose sulphur trioxide and pass into sulphates, e.g.

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

It, however, be specially noted that in aqueous solution the corresponding ion, S_2O_7, is not known. On solution, the pyrosulphates take up water and pass into the acid sulphates

$$Na_2S_2O_7 + H_2O = 2Na'HSO_4',$$

the process apparently proceeds so quickly that it has not yet been possible to distinguish between the solution of a pyrosulphate and an equally strong solution of the corresponding acid salt. From experience gained from other acids of a similar composition, however, cases are known in which differences can be detected between the ions of the normal and of the pyro acids.
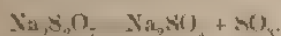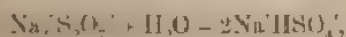
Thermochemical Relations.—The heat of formation of sulphur trioxide from its elements is 432 kj. Its heat of vaporisation is 48 kj., its heat of formation in the vapour form amounts, therefore to 383 kj. Since the heat of formation of the dioxide amounts to 297, this would, by combustion to the trioxide, develop 86 kj. In spite of this great heat evolution, this process takes place only very slowly and incompletely, and, in order to be of use for manufacturing purposes, it must be accelerated by catalysers, e.g. platinum.

The trioxide dissolves in water with great development of heat, amounting to 164 kj. Sulphuric acid, H_2SO_4, dissolves in water with development of 75 to 88 kj., at great dilution the heat effect still increases to a measurable extent. By the formation of sulphuric acid, therefore, from trioxide and water, about 85 kj. are developed.

The heat of neutralisation and sulphuric acid varies according as the acid or the normal salt is formed. If a mole of caustic soda is added to a mole of sulphuric acid in dilute solution, so that the acid salt is formed, $H_2SO_4 + NaOH = NaHSO_4 + H_2O$, 62 kj. are developed; the second mole of caustic soda yields the considerably greater evolution of heat, viz. 69 kj.

From the large amount of heat which is developed on dissolving sulphuric acid in water, one may conclude that the dissociation of the acid into its ions is accompanied by a greater development of heat. In the normal solutions used in the experiments, the first stage of the dissociation $H_2SO_4 = H + HSO_4'$ is fairly complete, and the second $HSO_4' = H + SO_4''$, has proceeded about half way. By the action of the first mole of caustic soda, the normal heat of neutralisation,

...phur to sulphuric acid—

...), - 6HCl.
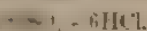
...logy can be destroyed
... It is therefore used to remove
...the fabrics bleached by
... action.   By reason of the

... thiosulphate, and any excess
...r, and spun materials of
... In the case of the dechlor...
... in excess of the salt genera...
... of writing paper and po...
A knowledge of this fact a...

... kind of oxidation by means
... according to the scheme

$$...O + 2NaI.$$

$$... + 2I$$

... but a new divalent an...
... called tetrathionic acid   The
... along with related s...
... the transformation of th...

... quickness and sharpness, a...
... analysis can be base...
... determined by means
... Further, the method o...
... substances which liberate...
... potassium iodide, e.g. chlorine...
... the determination of
... these to act on a know...
... and titrating the residu...

... only on the variety a the
... the fact that an acidifie...
... powerful reducing agent.
... oxidised by the free oxyg...
... the analyses just describe...
... state, but, in this case, the...
... quality of this solution i...
... less convenient and therefo...

ral solution, ... in the absence of hydrion, whereas it immediately
... gives decomposition in the presence of the latter. The reason of
... again to be sought for in the fact that in the second case more
... compounds can be formed, for whose formation hydrion is
...red.

305 Tetrathionanion.—The formation of the sodium salt of this
... the action of iodine on sodium thiosulphate has already been
...ed p. 300). For the purpose of preparing the free acid lead
...iphate is used. This is decomposed with the calculated quantity
...ine according to the equation

$$2PbS_2O_3 + 2I = PbS_4O_6 + PbI_2.$$
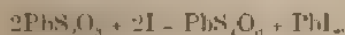
... as in the corresponding reaction with the sodium salt, there
...rmed lead tetrathionate and lead iodide. The former passes into
... the latter separates out. From the filtered solution, lead is
...itated as almost insoluble lead sulphate by the careful addition of
... sulphuric acid, while the tetrathionic acid remains in solution.
...he solution has a strong acid taste and reaction, and is much less
... than that of dithionic acid. Sulphur soon separates from the
... which simultaneously evolves sulphur dioxide and contains
...uric acid. The decomposition ensues according to the equation

$$H_2S_4O_6 + H_2O = H_2SO_3 + H_2SO_4 + 2S.$$
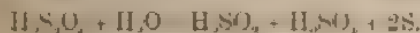
... **Pentathionic Acid.**—This is obtained by passing sulphuretted
...ogen into an aqueous solution of sulphurous acid. Whereas one
...ion of the substances simply undergoes transformation to sulphur
... water, according to the equation

$$2H_2S + H_2SO_3 = 3S + 3H_2O,$$
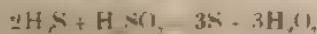
...her portion forms pentathionic acid and water, according to the
...tion

$$10H_2SO_3 + 5H_2S = 3H_2S_5O_6 + 12H_2O.$$
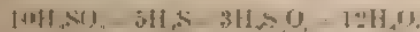
...aration, a portion of the sulphur can be separated. The other
...on, however, is present in such a fine state of division, in what is
...ed *colloidal solution*, that it behaves almost like a dissolved substance,
... is not retained by a filter. By preparing a salt of pentathionic
... from this solution, recrystallisation, etc., pure salts of pentathionic
... can be obtained. We can, however, not enter here on a description
...he very troublesome methods by which this object is attained.
Pentathionic acid is also unstable and readily decomposes into
...phurous acid, sulphuric acid and sulphur.
Solutions containing one of the higher polythionates undergo
...ormation in such a way that other thionates are produced.
...., the *trithionate* passes into *dithionate* and *tetrathionate*

$2Na_2S_2O_3 = Na_2S_4O$

therefore, very diffic

of dry chlorine b

a red-brown liquid

very unpleasant smell

composition is expressed

freezes at -80

of which it dissolve

can be again sep

The monochloride

water: the chlorine s

sulphur partly separate

sulphuric acids. The

with the amount of

represented by an

the arts for vulcanising

the latter becomes more

chloride, it is absorbed

the temperature and

compound SCl_2 was first

time, however, *sulphur*

to be a definite compound and

be assumed to be united to oxygen to form hydroxyl. The suitability of this assumption is seen from the fact that the actual reactions of this substance are in agreement with it.

Thus, in fact, derivatives of sulphuric acid are known which have the same relation to it as the metal chlorides have to the metal hydroxides, and which, therefore, support the assumption that in sulphuric acid hydrogen and oxygen are united together to hydroxyl.

* A "proof" of this assumption is *not* given by those compounds. The actual phenomenon is that the elements O and H are eliminated in the proportions OH, and Cl simultaneously enters. It cannot however, be asserted that these two elements, in order that they may be simultaneously eliminated, *must* previously have been *united*, for there are numerous cases in which such an assumption cannot be sustained. The sole purpose of this assumption, therefore, is to state that the reaction in question often and easily occurs.

* On such relations all the so-called "constitutional formulæ" of substances are based. These are a short expression for the chemical reactions actually observed. Since the latter, however, depend on other conditions besides the chemical nature of the substances, *e.g.* on temperature, pressure, presence of other substances,—it is to be anticipated that a definite constitutional formula can represent the behaviour of the given substance only within a definite range, and will prove all the less satisfactory the more deeply and comprehensively the chemical behaviour of the substance is known.

* Such diversity can, if necessary, be expressed by the assumption of several constitutional formulæ; but this is only a makeshift. For the complete representation of the chemical behaviour, a numerical characterisation of the mutual relations of all the transformation products of the substance would be necessary. From such a stand point, the chemistry of the present day is still very far removed.

If sulphuric acid be written as a hydroxyl compound, we obtain the formula $SO_2(OH)_2$. The atomic group SO_2 is called *sulphuryl*, and the two possible chlorine derivatives would have the following formulæ and names :—

$$SO_2(OH)Cl, \text{ Sulphuryl hydroxychloride,}$$
$$SO_2Cl_2, \text{ Sulphuryl chloride.}$$
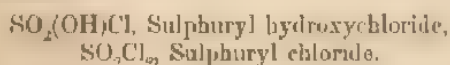
The first name is not used, as being too long; the first compound, which still contains one acid hydrogen, is called chlorosulphonic acid.[1]

Chlorosulphonic acid is obtained from sulphur trioxide and hydrogen chloride, which combine on being gently heated —

$$SO_3 + HCl = SO_2(OH)Cl.$$
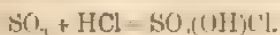
It forms a colourless liquid of density 1·7, and boils at 152 .

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[1] The name is due to the fact that in organic chemistry numerous compounds of sulphuric acid are known of the formula $R \cdot SO_2OH$ (where R is a compound "radicle"), which are called sulphonic acids.

Chlorosulphonic acid fumes in moist air, because it undergoes transformation with the aqueous vapour to difficultly volatile sulphuric acid and hydrochloric acid—

$$SO_2(OH)Cl + H_2O - H_2SO_4 + HCL$$
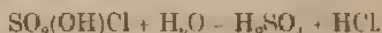
This reaction, viz., the re-formation of the original acid from its chloride by the action of water, is a general reaction of the acid chlorides.

* In this respect the acid chlorides differ essentially from the metal chlorides, with which they have a *formal* similarity (p. 305). Whereas metallic hydroxides undergo transformation with hydrochloric acid to metallic chlorides and water, the acid chlorides, on the other hand, undergo transformation with water to hydroxide and hydrochloric acid. The reaction, $RCl + H_2O - R . OH + HCl$, proceeds in the first case from right to left, in the second case from left to right.

* If, now, we remember that, in principle, no chemical reaction can be *complete*, we can say that the two cases differ from one another essentially in the fact that the one or other side of the equation of reaction predominates. Or, as we can say with reference to what was set forth on p. 250, the acid chlorides undergo almost complete *hydrolysis* with water.

* While the previous remarks dealt with the reactions of the particular substances with a small amount of water, the processes which take place on solution in much water must also receive special consideration. Under these conditions, ion formation can occur, and, in general, *those reactions take place in which specially stable ions are formed.* Among these, chloridion must, in the first place, be reckoned.

On decomposing chlorosulphonic acid with much water, there occurs the reaction

$$SO_2(OH)Cl + H_2O - 2H^.SO_4'' + H^.Cl',$$
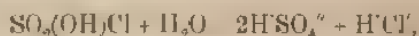
i.e. the ions of sulphuric and hydrochloric acids are formed. Since these two acids are largely dissociated into ions, i.e. form very stable ions, this reaction is practically complete.

The decomposability of the chloride by water is therefore increased, owing to the corresponding acid being able to form stable ions.

In accordance with these considerations, it must be regarded as possible that hydroxides exist which stand *between acids and bases* in such a way that the two sides of the equation of reaction to some extent counterbalance one another. They will, therefore, under certain conditions, act as *acids*, under other conditions, as *bases*. We shall soon have an opportunity of indicating such substances (Chap. XIII.).

The second chloride of sulphuric acid, sulphuryl *chloride*, SO_2Cl_2

produced by the direct combination of sulphur dioxide and chlorine. reaction does not take place very quickly, but is greatly accelerated, catalytically, by the presence of camphor (an organic substance). It obtained as a colourless, very mobile liquid, having the density 1·67 boiling at 69. The fact that the boiling point of sulphuryl chloride is so much lower than that of chlorosulphonic acid is an example of the general rule that the boiling point of the chlorine compounds is always considerably lower than that of the corresponding hydroxyl compounds. The same is seen on comparing chlorosulphonic acid (boiling point 152) with sulphuric acid (boiling point 340).

Sulphuryl chloride fumes only slightly in the air, because it reacts much more slowly with water than chlorosulphonic acid does. The compound is formed by the action of a small quantity of water $SO_2Cl_2 + H_2O = SO_2(OH)Cl + HCl$, with much water, sulphuric and hydrochloric acids are formed $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$.

As the decomposition of sulphuryl chloride by much water takes place much more slowly than that of chlorosulphonic acid, it looks as the former passed directly into sulphuric and hydrochloric acids without passing through the intermediate stage of chlorosulphonic acid. the chlorosulphonic acid which is formed undergoes decomposition quickly that at no time during the reaction can any considerable amount of it be detected.

Similar relations are often found. In all cases, therefore, where intermediate stages are apparently passed over, it must be in mind that they may escape observation owing to differences velocity of reaction, as in the above case.

Besides the two chlorides of sulphuric acid, a chloride of pyrosulphuric acid — pyrosulphuryl chloride, $S_2O_5Cl_2$, — is also known. It is formed by withdrawing the elements of water (by means of phosphorus pentoxide) from chlorosulphonic acid, $2SO_2(OH)Cl - H_2O$ $= S_2O_5Cl_2$. It is a liquid similar to chlorosulphonic acid, only more mobile and having a greater density. Its density is 1·82, and its boiling point 142. Its vapour, on being heated, decomposes into sulphur trioxide, sulphur dioxide, and chlorine.

With water, pyrosulphuryl chloride reacts in a manner similar to other chlorides of sulphuric acid. The reaction does not appear so violent as in the case of chlorosulphonic acid, because it takes place slowly.

H. Combining Weight of Sulphur

19. Since sulphur forms a large number of compounds which can analysed with exactness, very varying methods have been employed for the determination of this important combining weight. The most number was obtained by Stas by determining the ratio in which united with sulphur to form silver sulphide. On the other hand, determining the amount of silver which can be obtained from a

weighed quantity of silver sulphate, he obtained the data necess
for the independent calculation of the desired number.

For example, by heating 59·4225 gm. silver in sulphur vapo
68·2482 gm. of silver sulphide was obtained : the two weights ar
the ratio 1 : 1·1485.   Further, 81·023 gm. silver sulphate yiel
56·071 gm. silver on being converted to this by heating in a cur
of hydrogen, in accordance with the equation $Ag_2SO_4 + H_2 = H_2SO$
$2Ag$.   Since in silver sulphide, Ag_2S, the ratio of silver to sulphu
the same as in silver sulphate, there correspond to the amount of si
found, 64·3985 gm. silver plus sulphur, or 8·3275 gm. sulphur, and
remainder, 16·6245 gm., is oxygen.   Since in silver sulphate there
four combining weights of oxygen to one of sulphur, we have the p
portion $4 \times 16 : x = 16·6245 : 8·3275$, and $x = 32·06$.   The mean v
of all such determinations has given the same number, $S = 32·06$.

CHAPTER XIII

SELENIUM AND TELLURIUM

320. General —Similarly to the triad chlorine, bromine, and iodine, the elements of the sulphur group also form a trinity of similar substances whose properties vary regularly with increasing combining weight. The analogy of the combining weights is seen, in the first place, from the following table :—

Chlorine	.	.	35·45	Sulphur	.	.	32·06
Bromine			79·96	Selenium	.	.	79·2
Iodine	.	.	126·86	Tellurium	.	.	127·6

As can be seen, the combining weights of the corresponding members of the two groups are very nearly the same. Whereas, however, sulphur and selenium have rather *smaller* values than chlorine and bromine, the relation is reversed in the case of iodine and tellurium.

A similarity also exists between the two groups in the fact that the first elements in each, chlorine and sulphur, occur very widely distributed in nature, while the other two pairs are relatively sparingly found. Further similarities will become apparent in describing selenium and tellurium.

321. Selenium was discovered in the year 1817 by Berzelius in the deposit of a sulphuric acid manufactory at Gripsholm. It is an element which, like sulphur, can exist in different allotropic forms. Precipitated from aqueous solution, it is obtained as an amorphous red substance, and, with very dilute solutions, is got in the *colloidal* state, *i.e.* it is apparently in solution and passes through a filter.

From comparatively concentrated solutions, selenium is obtained as a bright red precipitate which, even under the influence of the temperature of boiling water, cakes together to a dense, black-red mass. At 17° selenium melts and forms a dark, viscous liquid which solidifies, on being quickly cooled, to an amorphous mass of a black-red colour, which breaks with a conchoidal fracture. If this amorphous selenium be kept some time at a temperature of 100° to 150°, it becomes crystalline and grey, with a somewhat metallic lustre. At 650° it boils.

Whereas the amorphous selenium does not conduct the elect

... in a measurable extent, the property of conductivity possessed by the crystalline form.

In this connection the special peculiarity is met with, that the electrical conductivity of crystalline selenium depends on the illumination which it experiences. Its conductivity is all the greater the stronger the light which it receives. On altering the strength of light, these changes occur in an exceedingly short time, and has therefore found practical application to the electrical transmission of signals. It has not yet been determined on what this peculiarity rests, but it appears that traces of foreign substances, and especially of the selenium compounds of the heavy metals mixed with selenium, play a great part.

In its compounds, selenium greatly resembles sulphur for selenium oxide, selenious acid, and selenic acid are not only analogously constituted to the corresponding sulphur compounds, but, in part, have a similar behaviour. From the special description of the different compounds, these similarities and differences will become apparent. The combining weight of selenium is Se = 79·2.

Hydrogen selenide, H_2Se, is a colourless gas with a very unpleasant smell, recalling that of decaying radish. It is very poisonous, and calls for special care in working with it. It readily dissolves in water in large amount. The solution has a feebly acid reaction, and in contact with the air red selenium quickly separates out, the hydrogen of the selenuretted hydrogen combining with the oxygen of the air to form water—$2H_2Se + O_2 = 2H_2O + 2Se$.

Hydrogen selenide is the hydrogen acid of selenium in the same sense as hydrogen sulphide is the hydrogen acid of sulphur. Its aqueous solution contains the ions Se'' and HSe', both of which are colourless. The salts of hydrogen selenide are the *metallic selenides*. By reason of the two combining weights of hydrogen, selenuretted hydrogen is H_2Se, and its salts, therefore, contain either two combining weights of a monovalent metal or one combining weight of a divalent one, etc. Selenuretted hydrogen can be obtained by action of stronger acids on metallic selenides. The method usually employed is to prepare ferrous selenide, FeSe, by heating selenium with iron filings and to treat this with hydrochloric acid. In a manner perfectly analogous to the preparation of sulphuretted hydrogen, ferrous chloride and selenuretted hydrogen are formed in accordance with the equation)

$$FeSe + 2HCl = H_2Se + FeCl_2.$$

From the solutions of the different heavy metals, selenuretted hydrogen precipitates the corresponding selenium compounds as insoluble mixtures. The compounds of selenium with the alkali metals are, however, readily soluble in water. In these they decompose similarly to selenuretted hydrogen, so that ...

...e time a red precipitate of selenium is deposited from their solu-
...s. This property is made use of for the purpose of obtaining or
...purifying selenium. The crude material is fused with sodium
...troxide (or with sodium carbonate, which acts in a similar manner),
...d the filtered solution of the melt is exposed in shallow vessels to
... air.

The poisonous action of seleniuretted hydrogen mentioned above,
...nds essentially on its ready decomposability by oxygen. Selenium
...reby separates out in the tissues in a finely divided form, and acts
...h. chemically and mechanically as an irritant.

3. Isomorphism.—The selenium which separates out under
... influence of the oxygen of the air on soluble metallic selenides is
...-alline, and, on closer examination, it is found to exhibit the same
...-alline forms as monoclinic (prismatic) sulphur, which separates
... from the fused mass. Further, elementary selenium occurs in some
... the naturally occurring kinds of sulphur; it is mixed uniformly with
...issolved in the sulphur, and imparts a rather dark, reddish colour
...it. Lastly, a large number of corresponding *compounds* of the two
...ments exist, having the *same crystalline form* and capable of forming
...ogeneous "*mixed crystals*," *i.e.* crystals the composition of which is
... governed by the laws of stoichiometry, but which, like that of
...tions, can exhibit every relation within definite limits. This is
...-trary to the ordinary behaviour of substances which otherwise
...-ays crystallise out side by side, so that *pure* crystals of *the one kind*
... found side by side with *pure* crystals of the *other* kind.

These facts are embraced under the conception of *isomorphism*
...-atity of form). In the first place, two substances are called
...-morphous when they have the same crystalline shape and can form
...-xed crystals. Thus sulphur and selenium are isomorphous in
...-pect of their monoclinic forms; for both elements not only crystal
... separately in like shapes, but when they together pass into the
...d state they form mixed crystals of varying composition, which is
...-termined essentially by the relative amounts of the two elements in
... mother liquor.

When one of the two isomorphous substances has the property of
...-stallising in different forms, the other substance has often the same
...-perty, and the different forms are alike in pairs. Thus it is to be
...-pected that there should be a rhombic form of selenium correspond
... to the rhombic form of sulphur, for such a relationship is found in
...ny other cases. Such a form of selenium, it is true, is not known,
... naturally occurring rhombic crystals of sulphur are found which
...-tain more or less selenium. Selenium is, therefore, capable of
...-ming mixed crystals with rhombic sulphur, and from this it may be
...-ferred as probable that a rhombic form of selenium exists, although
... perhaps so little stable under the conditions hitherto employed
... it has not *yet been possible to observe it.*

Elements which in the free state are isomorphous with one another, have the further peculiarity that their corresponding compounds with other elements are usually isomorphous. Thus, for example, almost all the salts of sulphuric acid have the same crystalline forms as the corresponding salts (i.e. containing the same metals and having a similar formula) of selenic acid. Such relationships are often found, and they are also sometimes met with in cases where no isomorphism of the elements is known. Hence a wider conception of isomorphism has been developed, and the term *isomorphous in the wider sense* is applied to those elements which, *while not themselves isomorphous, form isomorphous compounds of like constitution.* Of this kind of isomorphism, also, several examples will be cited later.

Since isomorphism and similarity of constitution go hand in hand, the fact of isomorphism can be used in doubtful cases to obtain a clue to the formulation of the compounds of new elements, i.e. to the choice of the most suitable combining weight from among the possible multiples (p. 141). In former times, especially, the relationships of isomorphism were of great service in this direction.

* In drawing such conclusions, however, it is necessary to carefully satisfy oneself that isomorphism is really present. Identity of the crystalline system and the possibility of expressing the forms of the two substances by the same crystallographic constants within the error of experiment, are not sufficient for the purpose, since chance agreement could not be excluded in this way. A sure criterion of an actual isomorphism is given if, along with the identity of shape, the property of forming mixed crystals can be demonstrated.

323. Selenious Acid.—When selenium is heated in the air or in pure oxygen, it takes fire and burns with a blue-white flame, forming selenium dioxide, SeO_2. At the ordinary temperature this compound, unlike sulphur dioxide, is not a gas, but a solid crystalline substance. Only on being heated does it volatilise, without melting, and pass into a vapour of the colour of chlorine.

Selenium dioxide, further, is formed by treating selenium with an oxidising agent. As a rule, it is obtained by heating selenium with nitric acid, evaporating to dryness, and subliming the residue.

Selenium dioxide dissolves in water and yields an acid liquid which contains selenious acid, H_2SeO_3. By evaporation, this compound can be obtained in transparent crystals which, on heating, lose water and pass into selenium dioxide.

Selenious acid is not a reducing agent like sulphurous acid. On the contrary, it readily gives up its oxygen, and elementary selenium separates out. Thus, for example, it is reduced even by the organic matter which is usually present in the dust of the atmosphere, and for this reason, the mouths of the vessels in which selenious acid is kept are generally covered with a crust of red selenium, and the preparation itself assumes, in course of time, a reddish coloration.

The reduction of selenious acid to selenium takes place very easily and smoothly by means of sulphurous acid, in accordance with the equation $H_2SeO_3 + 2H_2SO_3 = Se + 2H_2SO_4 + H_2O$. The selenium first separates out in the colloidal state, a red coloured, transparent liquid being formed. On standing some time, quickly if heated, selenium separates out as a brown red precipitate. This phenomenon can be used for identifying selenious acid and its salts.

Selenic Acid.—Powerful oxidising agents are required in order to convert the anion of selenious acid to the highest stage of oxidation of selenium, viz. the ion of selenic acid SeO_4''. The sodium salt is obtained by fusing sodium selenite with sodium nitrate. The latter yields up one combining weight of oxygen, by which the former is oxidised: $Na_2SeO_3 + O = Na_2SeO_4$.

The free acid is most easily obtained by treating silver selenite with bromine. Silver bromide and selenic acid are formed in accord with the equation $Ag_2SeO_3 + H_2O + Br_2 = H_2SeO_4 + 2AgBr$. In order to carry out this reaction, the silver salt is covered with water, and bromine added, with shaking, so long as its colour disappears.

The aqueous solution of selenic acid can be concentrated by evaporation, and a thickish liquid is finally obtained which has the density 2.6 and the general appearance of concentrated sulphuric acid. The pure acid solidifies to crystals which melt at 58°, the melting point is greatly lowered by quite small quantities of water. A crystalline hydrate, $H_2SeO_4 + H_2O$, melting at 25°, is also known.

Selenic acid is distinguished from sulphuric acid by its powerful oxidising action; it readily dissolves the noble metals and evolves chlorine with hydrochloric acid, thereby passing into selenious acid—$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O$. The salts of selenic acid are isomorphous (p. 311) with those of sulphuric acid, and also exhibit similar solubility relations. For example, its barium salt is just as difficultly soluble as barium sulphate, and the salts of the two acids may, therefore, be readily confounded. In order to identify selenic acid in presence of sulphuric acid, the liquid is previously treated with a reducing agent. The former is thereby reduced to selenious acid or selenium, while the sulphuric acid remains unchanged, and can be estimated as such.

Chlorine Compounds of Selenium.—Of the remaining compounds of selenium, *selenium tetrachloride* has still to be mentioned. It is a white, crystalline substance with the formula $SeCl_4$, and is easily prepared by heating selenium in a current of chlorine. On being heated, it is converted into vapour without previous fusion. With water it forms selenious and hydrochloric acids, in accordance with the equation $SeCl_4 + 3H_2O = H_2SeO_3 + 4HCl$.

Compared with sulphur tetrachloride (p. 304), which is exceedingly unstable compound, the corresponding selenium compound may be termed a very stable substance. This increase in the stability of the chlorine

compounds forms a marked contrast to the decrease of the stability of the corresponding oxygen and hydrogen compounds.

Besides selenium tetrachloride there also exists a selenium monochloride, Se_2Cl_2, corresponding to sulphur monochloride. This is a dark red-brown liquid from which, when heated, selenium tetrachloride escapes while selenium remains behind—$2Se_2Cl_2 = 3Se + SeCl_4$. The stability relations are, therefore, different here from what they are in the case of sulphur, where the tetrachloride decomposes into chlorine and monochloride.

326. Tellurium.—While iodine is very similar to bromine, if not in external appearance, at least in the nature of the corresponding compounds, the differences between selenium and tellurium are more pronounced, so that it has repeatedly been regarded as doubtful whether these two elements ought to be regarded as members of the same family.

Tellurium is a greyish white substance with a metallic lustre; its density is 6·1, and it conducts the electric current like a metal. It melts at 450°, and boils at 1400°. The vapour is only slightly denser than corresponds to the formula Te_2.

The *combining weight* of tellurium, Te = 127·6, is, as has already been mentioned, greater than that of iodine, whereas the combining weights of the other elements of this group are smaller than those of the corresponding halogens. Many investigations have therefore been carried out because it was believed that this deviation was due to incorrect determinations; it has, however, been found with certainty that the numbers are as stated.

Besides the metallic tellurium, there is also a black, apparently amorphous form, in which tellurium is obtained by precipitation from its solutions. It has a considerably smaller density.

Tellurium combines with the metals to form tellurides, these correspond to the sulphides in composition, and have generally a metallic appearance. The tellurides of the alkali metals are soluble in water, and form the ions Te'' and HTe'. From these tellurium separates out under the influence of the oxygen of the air.

Tellurium hydride, H_2Te, is obtained by the action of the strong acids on tellurides; it is a gas possessing an offensive smell and poisonous properties, behaves similarly to the hydrogen compounds of sulphur and selenium, and in aqueous solution is, like these, readily decomposed by the oxygen of the air.

Heated in the air, tellurium burns, forming the *dioxide*, which is a white substance volatile at a red heat. *Tellurous acid*, H_2TeO_3, is obtained by oxidising tellurium with nitric acid. It is a white mass, slightly soluble in water, and has only feebly acid properties. With strong acids, the compound behaves as a base, hydroxyl being eliminated and a salt formed. Compounds are hereby produced which are derived from a tetracid base, $Te(OH)_4 = H_2TeO_3 + H_2O$. T

ts are, however, also very unstable towards water, just as, in fact, substances which can act both as base and as acid yield in both es only slightly stable compounds

Tellurous acid can be converted into *telluric acid*, H_6TeO_6, by powerful oxidising agents. This has no similarity to sulphuric or nitric acid, for it forms a crystalline mass, difficultly soluble in water, and possessing feebly acid properties. The crystals which can be obtained from water have the composition $H_2TeO_4 + 2H_2O = Te(OH)_6$, and on heating, pass first into the acid H_2TeO_4, and then into the anhydride TeO_3. The latter is a yellow mass, which is indifferent towards water.

Telluric acid also exhibits basic properties.

Whereas, therefore, the oxygen compounds of tellurium agree in composition with those of sulphur and selenium, their *chemical behaviour* is very different. It is, it is true, a general phenomenon that the elements with higher combining weight form more feebly acid or more strongly basic compounds compared with the related elements of lower combining weight, but it is seldom that the phenomenon makes its appearance so abruptly as in the present case.

Finally, it has to be mentioned that tellurium combines with chlorine to form the compounds $TeCl_2$ and $TeCl_4$, and with bromine to form $TeBr_2$ and $TeBr_4$. These are crystalline substances, volatile without decomposition at moderately high temperatures, and resembling in properties the halogen compounds of the metals, *e.g.* of mercury.

CHAPTER XIV

NITROGEN

327. General. —As was shown on p. 36, there is present in the air, besides oxygen, another substance which constitutes the greater part both by weight and by volume. From the fact that the residue of the air after removal of the oxygen can support neither combustion nor life, it was called *azote*, but it is now called *nitrogen*. Its chemical symbol is N, from nitrogenium. This name is due to the fact that nitrogen is an essential component of saltpetre (nitrum). Its combining weight is N = 14·04.

The properties of nitrogen are essentially those of the air minus those due to oxygen. Thus, it is colourless, odourless, and only slightly soluble in water. Its molar weight is 28 ; as gas, therefore, it has the formula N_2. It is distinguished from oxygen essentially by the fact that it is capable only in a very slight degree of reacting chemically with other substances. There are only very few substances which can unite directly with nitrogen. If, however, the nitrogen has passed into combination, the substances which are formed show a very considerable variety and power of transformation, so that the range of nitrogen compounds is a large and important one.

Compounds of nitrogen are of frequent occurrence both in the mineral and, more especially, in the organic kingdoms. Of the former there may be mentioned the important groups of *nitric acid* and *ammonia*; these will presently be discussed in detail. In the organic kingdom, nitrogen is in so far of especial importance as the substances with which the phenomena of life are directly connected, and whose presence appears to be necessary for the processes of life, viz., the *albuminoids*, all contain nitrogen.

328. Preparation and Properties. —In order to obtain nitrogen, it is only necessary to free the ordinary air from the oxygen it contains. For this purpose, metals are most suitable which combine with oxygen and yield solid, non-volatile oxides. The choice is somewhat limited, from the fact that those metals which decompose water must be excluded. These would form hydrogen from the traces of water

our present, and this would contaminate the nitrogen, and could be separated from it only with difficulty. The necessary conditions are at found united in *copper*.

If a current of air be passed through a tube filled with copper in the form of turnings or of thin wire, and raised to a medium red heat, it yields up all its oxygen to the copper and nitrogen escapes and can be collected over water (Fig. 92). A colourless gas is obtained, with which it is easy to demonstrate the property that burning substances, not only wood but also sulphur and phosphorus, are extinguished in it.

The *density* of the nitrogen so obtained is rather greater than that of nitrogen prepared from its compounds by chemical reactions. This, at first, puzzling phenomenon has been explained by the fact that besides nitrogen, there is present in the air a heavier gas which combines with copper just as little as nitrogen does, and therefore remains mixed with this. This was separated in the pure state from
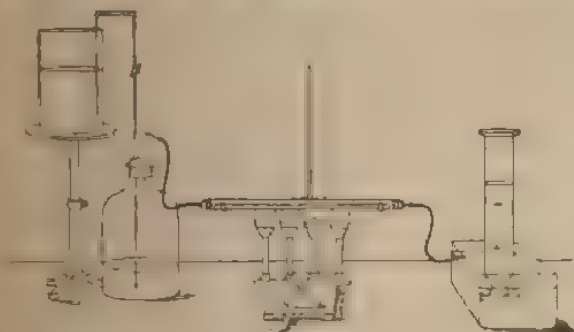
Fig. 92.

atmospheric nitrogen by Rayleigh and Ramsay in 1894, and has been found to be an elementary substance. It has been called *argon*.

The density of pure nitrogen stands to that of oxygen very nearly in the ratio 7 : 8. Nitrogen is, therefore, the lighter component of the air, and, therefore, lighter than this itself.

At -194°, nitrogen can be condensed under atmospheric pressure to a colourless liquid, which at -214° passes into a solid, ice-like substance.

If the temperature is higher than -146°, gaseous nitrogen cannot be made to assume the liquid state by any pressure; -146° is, therefore, the *critical temperature* of this substance. The *critical pressure*, or, the pressure at which, slightly below -146°, condensation can still be effected, amounts to 35 atm.

Chemical criteria, by means of which gaseous nitrogen can be constantly distinguished from other gases, scarcely exist. In general, one is content to regard as nitrogen, gases which are neither combustible nor support *combustion*, and which do not combine with metals,

phosphorus, and the other reagents for gases which are in use. Since as has been mentioned, free nitrogen has little tendency to take part in chemical reactions, it is generally of no great importance whether nitrogen is present or not; it acts only as an indifferent diluent to the other gases with which it is associated.

If nitrogen, under a small pressure, is rendered luminous by an electric discharge in a tube arranged for that purpose (p. 97) a spectrum of numerous lines is observed which is more especially characterised by the appearance of bands shaded away on one side. These consist of numerous fine lines which, on the one side, are close, crowded together, and on the other side are regularly arranged further and further apart. By means of this phenomenon, the presence of nitrogen in gases can be recognised with comparative ease.

329. **The Air.**—Although the air by which we are surrounded is a mixture, it has to be taken into account in so many phenomena that a special discussion must be devoted to it here.

Air consists, in round numbers, of 0·21 parts of oxygen and 0·79 parts of nitrogen, by volume. If these volumes are multiplied by the densities of the two gases and divided by the sum of the two numbers, we obtain as the proportions by weight 0·23 and 0·77 respectively. The numbers are not perfectly constant, since processes are continually taking place in the air which tend to alter this ratio. Close investigation has, however, shown that the differences which actually occur move within very narrow limits about the mean values, oxygen 0·21, nitrogen 0·781, argon 0·009 parts by volume.

The influences which tend to alter the composition of the air consist, on the one hand, in the *withdrawal of oxygen* by oxidations of all kinds, *i.e.* by rapid and slow *combustions*. On the other hand, *green plants* have the property of giving off oxygen to the surrounding air, and the almost constant composition of the air which is observed is an expression of the fact that these two opposed actions exactly counterbalance one another.

If one considers now, that the processes by which oxygen is removed are concentrated in the large towns, where, conversely, the evolution of oxygen is very small, whereas, on the other hand, the evolution of oxygen by green plants occurs only in summer and during the day, one might expect much greater differences than actually occur. The cause of the equalisation is to be found in the great movements which the ocean of air constantly undergoes. By reason of these the one-sided actions do not take place on one and the same isolated portion of air, but are distributed over large and varying amounts which stream past over these different localities. These movements also produce an effective *mixing* of the different portions of the air, and the comparative constancy of the composition of the atmosphere is the result.

On account of the fact that the ratio of the volumes approximates

round number 1 : 4, the supposition has sometimes been
d that the air is a *chemical compound* of the two elements.
is wrong, for the properties of the air are those which follow
properties of its components on taking into account the pro-
of mixing. A chemical compound, however, is characterised
ct that its properties are essentially different from the corre-
mean values of the properties of its components.
example, air alters in composition on being dissolved in
ce oxygen dissolves to a larger extent than nitrogen. The
s in which the two elements are present in water saturated
are 0·35 oxygen to 0·65 nitrogen. Further, the components
r can be separated by diffusion (p. 93), although not very
ly, since the two densities are fairly close to one another.
es the two gases mentioned, the air also contains as regular
ts *water vapour, argon,* and *carbon dioxide.* With regard to
the necessary data have already been given (p. 125); the
stances will be discussed later.
analysis of the air can be performed in many ways. The
escribed above (p. 317) can be developed to a quantitative one,
ed in Fig. 92. This is done with greatest accuracy by bringing
to a space shut off by mercury, measuring the pressure, tem
and volume, and then removing the oxygen by means of a
copper wire raised to a red heat by an electric current. After
the three magnitudes are again determined, and by this means
relation is obtained.
93 an apparatus con-
for this purpose is

d of glowing copper,
us can be used. This
advantage that it re-
he oxygen very com-
rom the air even at
ary temperature. The
as is introduced in the
thin rods into a glass
of the form *A* (Fig. 94),
also completely filled
er to the point *a*
to be investigated is
in a graduated tube,
burette *B*, which is
ted with the *absorption*
by means of a narrow
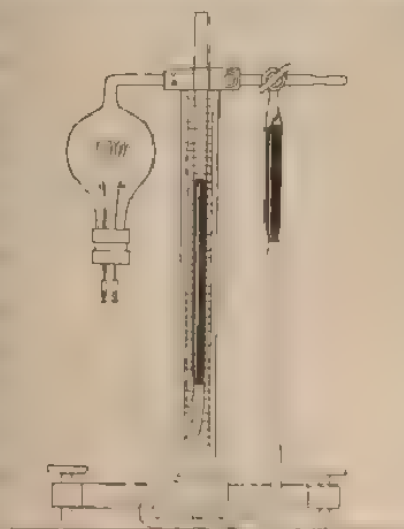raising the pressure
which is *filled with water,* the water is forced over to

the phosphorus. When the absorption of the oxygen is complete, the nitrogen is returned to the gas burette by the reverse process, and is th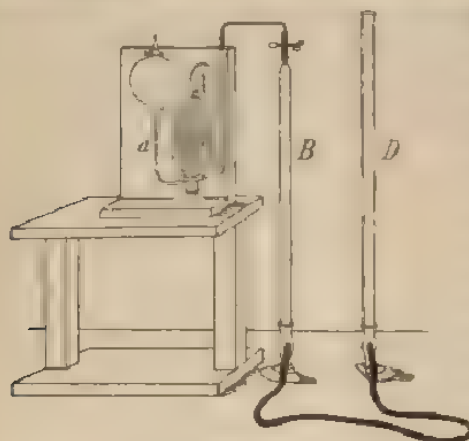ere measured after the atmospheric pressure has been re-established by bringing the water level in B and D to the same height.

FIG. 4.

A third method, given more than a hundred years ago by Volta (the inventor of the voltaic pile), depends on the combination of oxygen with hydrogen. The air is placed over mercury in a graduated tube, into the upper end of which two platinum wires are fused; the volume, pressure, and temperature are measured, and *hydrogen* then added. By repeating the measurement, the total volume is ascertained. On allowing an electric spark to pass through the mixture, the oxygen combines with the hydrogen, and the former entirely disappears if sufficient hydrogen has been added. If the gaseous residue is now measured, $\frac{2}{3}$rds of the volume which has disappeared consists of hydrogen, $\frac{1}{3}$rd of oxygen. The amount of oxygen, by volume, in the air examined is, therefore, obtained by dividing the diminution of volume, after explosion, by 3.

Great importance was formerly attached to the determination of the amount of oxygen in the air, because it was believed that on it depended the good or ill health of man and beast. The fact, however, that the variations which occur are very small, and that the volume concentration of the oxygen in the air is altered much more than the amount of these variations by the comparatively small changes in the pressure of the air and in the amount of vapour it contains at different times and at different heights, has led to the conviction that such influences are not appreciable; the analysis of the air has thereby lost much of its former interest.

330. **Oxygen Compounds of Nitrogen.** —The number of compounds which oxygen (partly along with hydrogen) is capable of forming with nitrogen, is very great. Instead of treating these strictly systematically according to their composition, it will be more expedient to first consider the most important and most widely distributed of them, from which the majority of the compounds are formed. These are *nitric acid* and its salts, the *nitrates*.

Nitric acid is an acid of the composition HNO_3; it contains the colourless, monovalent nitranion, NO_3. Its occurrence in the free state in nature is exceptional, for the reason that it is a strong acid, and therefore, at once forms salts. All the more frequent and widely distributed are the salts of nitric acid, or the nitrates. *Saltpetre*, or *potassium nitrate*, KNO_3, has been known from ancient times, and occurs in the earth in places where nitrogenous animal substances, especially animal excremental matter, is subjected to the action of the atmospheric oxygen. It can be readily obtained by extracting the soil with water and evaporating the solution. *Sodium nitrate*, $NaNO_3$, known as *Chili saltpetre*, is found accumulated in the rainless districts of Chili, and serves as the most important source of nitric acid and of its derivatives. Finally, it has to be mentioned that the nitrogen, oxygen, and water in the air can, under the influence of electrical processes, combine to nitric acid, which is, therefore, not infrequently found in the form of its salts in rain water, although in very small amounts.

Pure nitric acid, HNO_3, is obtained by distilling its salts with sulphuric acid. The corresponding sulphate is formed, and the nitric acid, which is readily volatile, can be distilled off from the non-volatile. With sodium nitrate, the reaction takes place according to the equation

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4 .$$
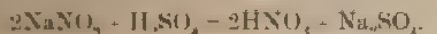
In this case, also, the process takes place in two stages; acid sodium sulphate is first formed (p. 293), $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$, and the other reaction, $NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3$, takes place only at higher temperatures. Since at the temperature necessary for this the nitric acid is unstable and decomposes into other substances, it is usual to take the components in accordance with the former partial reaction, nitric acid being obtained along with acid sodium sulphate. Likewise, it is customary to add a little water to the sulphuric acid, as aqueous nitric acid does not decompose nearly so readily when heated as the anhydrous acid.

However, by carrying out the distillation in a rarefied atmosphere at a lower temperature (p. 160), the above disadvantages can be avoided. In the manufactures, almost pure nitric acid is prepared on the large scale at the present day by distillation under reduced pressure.

Pure nitric acid is a colourless liquid, with a density 1·56, and boils at 86. It does not keep well, for even under the influence of light, it decomposes into oxygen and lower (i.e. containing less oxygen) oxides of nitrogen, which dissolve with a yellow colour in the rest of the acid. Addition of water makes it much more stable. The cause of this is the same as that previously given in the case of perchloric acid (p. 222), *nitric acid has a great tendency to form ions*, and, there

fore, processes by which water is produced from the acid, take pla
with especial readiness. This is what occurs in the decomposition o
nitric acid under the influence of light, for the hydrogen of the ac
thereby passes into water.

On adding increasing quantities of water to the acid, the boili
point of the latter rises not only to that of water but considerabl
higher. The highest boiling point, 120 under atmospheric pressure
is possessed by the 68 per cent acid. On further addition of wate
the boiling point again sinks, and ultimately reaches that of water

The relations which obtain here are therefore perfectly similar t
those in the case of hydrochloric acid (p. 184). In this case also, th
mixture of 0·68 nitric acid and 0·32 water, which correspond
approximately, to the formula $2HNO_3 + 3H_2O$, must not be regarde
as a chemical compound, for its composition changes with the pressur
In this case, indeed, the acid is all the more concentrated the high
the pressure under which the distillation proceeds.

331. The Chemical Properties of Nitric Acid.—The propertie
which are possessed by nitric acid, *as an acid*, must be distinguishe
from those which pertain to it in respect of *other* decompositions
The former depend, as has previously been explained (p. 245), essent
ally on the degree of electrolytic dissociation; the others, howeve
depend on the composition and the stability of the anion, and of th
undissociated acid.

With regard to the first point, nitric acid belongs to the stronge
acids, and, in this respect, ranks along with hydrochloric acid. Accor
ingly, even at great dilution, it has an acid taste and reddens litmu
Likewise, it readily attacks and dissolves metals. In this case, how
ever, hydrogen is frequently not liberated, but combines with th
oxygen of the nitric acid to form water, corresponding reduction pro
ducts being thereby formed

Since the dissociation increases with dilution, the general aci
properties of this substance will become most prominent in dilut
solutions, whereas, on the other hand, the specific actions which hav
just been mentioned will be chiefly found in concentrated solutions

As can be gathered from the statement made above, that pur
nitric acid decomposes even under the influence of light, this subst nc
belongs to the same type of compounds as ozone and hydroge
peroxide, viz. compounds which can give up oxygen and pass int
more stable substances, and which, therefore, act as strong *oxidisi
agents*. As a matter of fact, this is the most prominent property o
nitric acid, and most of its applications depend on it.

This property of nitric acid first became known in the case of i
action on the metals. There are a number of metals, such as coppe
mercury, and silver, which are not dissolved by dilute acids On th
other hand, they are precipitated from their salts by hydrogen Th
cause of this lies in the very different conditions under which chemic

equilibrium between the metals, the hydrogen and the ions, is established. Since a substance acts all the more strongly, i.e. has a greater tendency to disappear as such, the more concentrated it is, it can be argued that all metals will be precipitated from their salts by hydrogen, if this is employed in suitable concentration. Such a reaction as $H_2SO_4 + Zn = ZnSO_4 + H_2$ could then be reversed, so that zinc and sulphuric acid would be produced from zinc sulphate and hydrogen.

The different metals, now, are distinguished by the different concentrations of hydrogen required for such a reaction. Whereas, in the case of zinc, it would require to be very great, since, indeed, the decomposition of the acids by this metal takes place so easily, it would, on the other hand, be very small in the case of silver, for hydrogen, under the ordinary pressure, and therefore of the correspondingly small concentration, is sufficient to precipitate silver in the metallic state from its salts. All the metals can, accordingly, be arranged in a series beginning with the metal which requires the greatest concentration of hydrogen for its precipitation, and ending with that which is in equilibrium with the most dilute hydrogen. This series would be most naturally divided into two parts at that point at which the concentration of the hydrogen corresponds exactly to one atmosphere. This is, it is true, an arbitrary choice, but it corresponds to by far the largest number of cases in which the behaviour of the metals is tested comes into question.

In the first division, that of the metals which evolve hydrogen, we, in the first place, all the light metals, and, of the heavy metals, those belonging to the iron group. The heavy metals of the other series belong chiefly to the second division, but tin is an exception, and lead stands on the border. These relations will be more fully discussed under the different metals.

Those metals, now, which are not dissolved by dilute acids with evolution of hydrogen, are, for the most part, readily dissolved by nitric acid. This is due to the fact that the nitric acid converts the hydrogen which is first formed in the action, although only in immeasurably minute traces, into water by oxidation, and removes it, therefore, from the sphere of action. In other words, its action is to maintain an exceedingly small concentration of hydrogen, and thereby make it possible for more of the metal to pass into solution.

There are also some metals, such as gold and platinum, which are not dissolved by nitric acid. This depends on the fact that even the small concentration of hydrogen obtained by means of nitric acid, is too great to allow of a reaction taking place in the sense of a displacement of hydrogen. In order to dissolve such metals, stronger oxidising agents are required, by which a still smaller concentration of hydrogen is achieved.

of oxygen of these may is produced from the acid, take place ... of these may a vapour. This is what occurs in the decomposition of ... may and that by means of ... or the hydrogen of the ...

In adding ... quantities of water to the acid the boiling point ... is after ... to ... a water but considerable ... The liquid ... ... by most atmospheric pressure ... amount of the ... of the ... its heat. On further addition of water its boiling point ... and ultimately reaches that of water.

The boiling effect which here are therefore perfectly similar to those in the case of ... acid in ... In this case also, the mixture of ... nitric acid and ... water, which corresponds ... to the formula $HNO_3 + 3H_2O$ must not be regarded as a chemical compound, for its composition changes with the pressure. In this case, indeed, the more concentrated the higher the pressure under which the distillation proceeds.

The Chemical Properties of Nitric Acid. —The properties which are possessed by nitric acid in ... must be distinguished from those which pertain to it in respect of other decompositions. The former depend, as has previously been explained (p. 245), essentially on the degree of electrolytic dissociation; the others, however, depend on the composition and the stability of the anion, and of the undissociated acid.

With regard to the first point, nitric acid belongs to the strongest acids and, in this respect, ranks along with hydrochloric acid. Accordingly, even at great dilution, it has an acid taste and reddens litmus. It also ... ... marble and dissolves metals. In this case, however, ... hydrogen is generally not liberated, but combines with the oxygen of the nitric acid to form water, corresponding reduction products being thereby formed.

Since the dissociation increases with dilution, the general acid properties of this substance will become most prominent in dilute ...

...real, since other oxidising agents (e.g. chloric acid) also decolorise ...

An unmistakable test consists in the dark coloration produced by ... salts in liquids containing nitrates. The theory and practical ... of this reaction will be given somewhat later in connection ... the compound here in question, viz. nitric oxide.

Nitrogen Pentoxide. If pure nitric acid be treated with ... drating agents, it loses the elements of water and passes into ... anhydride (p. 213), in accordance with the equation
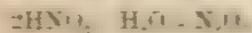
$$2HNO_3 - H_2O = N_2O_5.$$

To effect this reaction it is not sufficient to use sulphuric acid, but ... most powerful desiccating agent known, viz. phosphorus pentoxide, ... be employed. This substance, which we shall soon describe more ... is a white, snow-like powder, obtained by burning phosphorus ... air. If this is added to nitric acid contained in a retort, and ... mixture distilled after some time, the anhydride of nitric acid ... over as a mobile, very volatile liquid, which soon solidifies to ... white, crystalline substance, melting at 30°. This is exceedingly ... ... and decomposes spontaneously into oxygen and nitrogen ... oxide $2N_2O_5 = 4NO_2 + O_2$. The decomposition, also, is not pre... ... by sealing up the substance in tubes and thus protecting it ... the action of the air; such tubes usually explode after some ... when the pressure of the gaseous products of decomposition has ... me great enough.

Nitrogen pentoxide dissolves in water, with formation of nitric ... the process expressed in the above equation taking place in the ... sense

Thermochemical.—The heat of formation of solid nitrogen ... oxide is 55 kj, that of the gaseous, zero. On dissolving in water, ... are developed, two moles of dilute nitric acid being thereby ... ... We have, therefore, the equation $2N + 5O_2 + aq$ ... aq $= 2 \times 125$ kj. If it is desired to refer the heat of formation ... ... acid to the elements hydrogen, oxygen, and nitrogen, the ... of formation of water, $2H_2 + O_2 = 2H_2O + 2 \times 286$ kj, has to be ... ... and there is obtained

$$H_2 + N_2 + 3O_2 + aq = 2HNO_3, aq. + 411 \, kj.$$

... heat of formation of one mole of dilute nitric acid from hydrogen, ... oxygen, and water, is, therefore, 205 kj.

Nitric Oxide.—Lower oxides of nitrogen are formed by the ... of nitric acid on copper or other metals. The nature of this ... has already been explained; it depends on the fact that the ... drogen of the nitric acid which is replaced by the metal combines ... the oxygen of another portion to form water. Various products ... reaction are here formed, according to the metals, the temperature,

is peculiarity of nitric acid of dissolving silver but of leaving
unattacked, is used for the separation of mixtures or alloys of
no metals . on treatment with nitric acid the silver passes in
a, whereas the gold remains undissolved. On account of b
t power, this acid was called *aqua fortis* by the alchemists.

These metals which, like zinc and magnesium, dissolve in dilu
with evolution of hydrogen, are also dissolved by nitric acid
to of the fact that they are dissolved, the evolution of hydrog
se cases appears greatly diminished. This also is due to th
at the hydrogen combines with the oxygen of the nitric acid
rater ; in this case, however, the removal of oxygen goes furthe
t place of the brown, gaseous products of reduction, compoun
ogen are formed which contain hydrogen. These have les
ties, and remain, therefore, dissolved in the acid liquid, wit
ion of salts The last product of this reaction is ammoni
will be discussed further on.

8. The Salts of Nitric Acid.—Nitric acid is a monobas
and forms only one class of salts, namely, monovalent metal
ts of the formula MNO_3, divalent metals, salts of the formu
).. etc These salts can be formed in all the ways we have se
in which salts are formed ; for example, by the action of n
ases or hydroxides.

nitrates all have the property of being more or less read
in water, so that no precipitation reaction is known for
By reason of the large amount of oxygen they contain ,
ate when thrown on incandescent charcoal, *i.e.* the charco
at the expense of the oxygen of the nitrate, rapid com
tained with vivid production of light. The oxyge
the heat, for although the nitrates are much more stab
. they all exhibit the property of decomposing a
ten temperatures with evolution of oxygen, the met
remaining behind as oxide

mportant applications of the nitrates, also, depend u
with which they give up oxygen These will be con
the salts under the respective metals.

id o   also, of nitric acid and of the nitrates depen
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, viz.   cid, the copper is oxidised, and b
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cid, and mo   estigated with so
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band, they are p.   when heated, the prese
of this lies in the   e test is, however, not

...cal, since other oxidising agents of nitric acid also decolorise
...

...n unmistakable test consists in the ... coloration produced by
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...the process expressed in the above equation taking place in the
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334. Thermochemical. — The heat of formation of solid nitrogen
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...of formation of water, $2H_2 + O_2 = 2H_2O + 2 \times 289$ c, has to be
..., and there is obtained

$$H_2 + N_2 + 3O_2 + aq \quad 2HNO_3 \ aq + 411 \ c$$

...heat of formation of one mole of dilute nitric acid from hydrogen,
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...has already been explained; it depends on the fact that
...gen of the nitric acid which is replaced by the metal comb
...the oxygen of another portion to form water. Various prod
...duction are here formed, according to the metals, the temperatu

the vapour is black-red and almost opaque even in thin layers. On lowering the temperature and increasing the pressure, the former pale colour returns.

* These relations can be easily made clear by filling two small tubes of about 2 cm. diameter with the vapour of nitrogen peroxide under the same conditions, sealing them off, and heating one of them. Whereas the tube which is kept at the ordinary temperature appears pale brown in colour, the heated one soon acquires a pronounced dark colour. The comparability of the two tubes is assured by the fact that, under these conditions, both contain the same amount of substance independent of the temperature.

These phenomena are explained by the fact that there are two different compounds of the same composition, which are polymeric, the one containing twice as many combining weights of the two components as the other. In accordance with the density, the former has the formula NO_2, the other N_2O_4. The former is dark coloured, and is formed at a high temperature and under a small pressure; the latter is almost colourless, and is formed from the former under the opposite conditions. Under all circumstances, the vapour of nitrogen peroxide is a mixture of the two forms, and the relative amounts of these can be calculated from the density of the vapour.

* Thus, at 50° and 49·8 cm. pressure, the molar weight D has been found equal to 62. If x be the fraction of the total amount by volume formed by NO_2, that formed by N_2O_4 is equal to 1 $-x$, and a mixture of the two has a molar weight D $= 46x + (1 - x)92$. Hence, $x = \dfrac{92 - D}{46}$, from which, substituting the value of D, $x = 0.65$. Under the above conditions, therefore, the vapour contained 0·65 volumes of the simple compound and 0·35 volumes of the double compound. Since the weight of the latter is equal to 0·70 volumes of the simple one, the fractional amount of the simple compound by weight is $\dfrac{0.65}{0.65 + 0.70} = 0.48$.

There exists, therefore, between the two forms NO_2 and N_2O_4 a *chemical equilibrium*, in consequence of which the relative quantities of the two forms are determined by the temperature and pressure. If two of these magnitudes are given, the third is also fixed, *i.e.* at a given temperature and a given pressure only one definite ratio can exist between the two components. On the other hand, a perfectly definite temperature is required if it is desired to obtain under a given pressure a given ratio between the components.

The law which this equilibrium obeys is expressed by the formula

$$a^2 b = k,$$

where a denotes the concentration of the form NO_2 and b that of

from N_2O_4, L is a magnitude which is dependent on the temperature, or which, at constant temperature, is constant. It is, therefore, also called the *equilibrium constant*.

By *concentration* is understood the calculated amounts in moles of the substances present, divided by the volume measured in cc.

The above equation shows that when the concentration of the two forms is diminished by increasing the total volume, the ratio of their amounts does not remain unchanged. For example, if the volume is so much increased that a diminishes to half its value, b must also diminish, not to half but to a fourth, in order that the equation may be fulfilled. In other words, on increasing the volume, i.e. diminishing the pressure, a portion of the form N_2O_4 must change into NO_2, as was stated above as the result of experiment.

If we reflect that by the change just mentioned of the more dense into the less dense form, the pressure must become greater than it would be if this change did not occur, we see that the formula stated here is a restatement of the law which was given in a qualitative form on p. 234, namely, *when a system undergoes change, the process sets in which opposes this change.* If the pressure is diminished, a portion of the denser gas decomposes and again partially cancels the diminution of pressure. On the other hand, if the volume is diminished, the pressure does not increase in the same proportion as a single gas, but a portion of the NO_2 polymerises to N_2O_4, and the pressure cannot become so great.

Further, it has been established that heat is developed in the combination of NO_2 to N_2O_4. In accordance with the same principle, therefore, if the temperature be raised, that process will occur which opposes the rise of temperature, i.e. N_2O_4 will decompose into NO_2, because this process absorbs heat. This conclusion is also borne out by experiment.

The preparation of nitrogen peroxide can be carried out by means of a method already mentioned (p. 326), by converting nitric oxide into peroxide by means of free oxygen. The brown vapours obtained by the action of nitric acid on metals, after having been dried, are passed along with oxygen through a freezing mixture, the current of oxygen being so regulated that it is present in excess. The substance obtained can be easily purified by re-distillation.

For the preparation, also, use is made of the decomposition which the metallic nitrates undergo when heated. Lead nitrate, for example, gives nitrogen peroxide, according to the following equation —

$$2Pb(NO_3)_2 = 4NO_2 + O_2 + 2PbO.$$
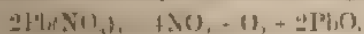
As has been already mentioned, the peroxide dissolves in water. In this process, however, it does not remain undecomposed, but reacts with the elements of water to form nitric and nitrous acids—

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$
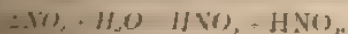
* The heat of formation of nitrogen peroxide in its simplest form NO_2 amounts to -32 kj; it therefore absorbs energy in its formation. In passing into the other form, N_2O_4, heat is developed: $2NO_2$, $N_2O_4 + 54$ kj.

337. **The Law of Mass Action.**—The relationships which have just been set forth form a special case of a general law which governs all chemical states of equilibrium. It can be expressed in the following form:

Let a chemical reaction between m_1, m_2, . . . moles of the substances A_1, A_2 . . . and n_1, n_2, . . . moles of B_1, B_2, . . . be represented by an equation of the form

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \quad n_1B_1 + n_2B_2 + n_3B_3 + \ldots,$$

then equilibrium will exist when the concentrations a_1, a_2, a_3, . . . b_1, b_2, b_3, . . . of the reacting substances have acquired certain values. These values are given by the following equation:—

$$\frac{a_1^{m_1} . a_2^{m_2} . a_3^{m_3} \ldots}{b_1^{n_1} . b_2^{n_2} . b_3^{n_3} \ldots} = k.$$

The concentrations of the substances standing on the one side of the reaction equation, therefore, appear in the numerator, and those of the substances on the other side, in the denominator, of the fraction, and each concentration appears as a factor as many times as the number of the moles with which the particular substance takes part in the reaction. It is here presupposed that the reaction equation is written in molar formulæ. The magnitude k is constant at a given temperature, i.e. it is independent of the absolute value of the concentrations, but changes with the temperature.

Only *gaseous* and *dissolved* substances can have varying concentrations. In the case of *solid* substances and *homogeneous liquids*, the concentration changes so little with the pressure that its influence is scarcely appreciable. For this reason, in all cases where solid substances and homogeneous liquids take part in an equilibrium, the corresponding members occurring in the fraction on the left of the equation become constant, and can be brought over to the right hand side, where they form all together a product which is constant for constant temperature.

This simple equation is the foundation of the whole theory of chemical equilibrium, and is applied in all cases where such questions have to be treated.

* As an example of its application, the more exact discussion of the case mentioned on p. 100 may be given; this deals with the chemical equilibrium between water vapour, iron, iron oxide, and hydrogen. The oxide of iron formed has the formula Fe_3O_4, and the equation, therefore, runs—

$$4H_2O + 3Fe \quad 4H_2 + Fe_3O_4.$$
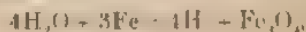
and the equation of equilibrium—

$$c_1^4 a_2^3 b_1^4 b_2 = k.$$

Here, however, a_1 and b_2 refer to solid substances (iron and iron oxide), and are, therefore, constant. On bringing them over to the right, there follows, $a_1^4 b_1^4 = b_2 k c a_2^3$, or, extracting the fourth root and putting the expression $\sqrt[4]{k b_2 a_2^3}$ equal to K, we obtain $a_1 b_1 = K$. That is to say, the ratio of the concentration (or the partial pressure) of the water vapour and the hydrogen must, at a given temperature, have a constant value, or, the two concentrations must be proportional. This is exactly what has been given by experiment.

338 **The Influence of Temperature on Chemical Equilibrium.** The view is often found very wide-spread that at a very high temperature all chemical compounds must decompose into their components, and that at places, therefore, where such a temperature prevails, e.g. on the sun, the chemical elements can exist side by side only in the *uncombined* state.

On questioning experiment and the theory which has been developed on the basis of the general laws of energy, another answer is given by both. By applying the general principle of movable equilibrium, which states that whenever an equilibrium is compelled to change, processes occur which oppose the compelling force, we must say that at higher temperatures that reaction will occur which opposes the rise of temperature, i.e. *which absorbs heat*. If all chemical decompositions took place with absorption of heat, the view cited above would be correct. There are, however, numerous substances (and to these the oxygen compounds of nitrogen almost all belong) which are formed from their elements with absorption of energy. It is just at higher temperatures that such compounds become more stable, and they cannot, therefore, be decomposed by heat.

Numerous examples of this general law are known. Thus, the vapour pressure of every liquid increases with rise of temperature, i.e. more liquid evaporates into the given space because the evaporation takes place with absorption of heat. If a liquid should ever be found which passed into vapour with *development* of heat, it would also necessarily have the property that its vapour pressure would *diminish* with rise of temperature.

On considering the equation of equilibrium on the preceding page, from this point of view, it can be said that, with a rise of temperature, those substances must increase which are formed with absorption of heat from the substances on the other side of the equation action. From this it can always be seen in what sense a c equilibrium will be shifted with rise of temperature.

In the example cited above, heat is developed by the ac water vapour on iron; conversely, water vapour is formed fro

oxide and hydrogen with absorption of heat. Consequently, with a rise of temperature, the ratio of water vapour to hydrogen must increase, or, as the temperature rises, the decomposing action of the iron on water vapour becomes less and less. This result, also, was given by experiment before the theory was known.

This qualitative principle has also been brought into a form suitable for calculation. We shall, however, refrain from the deduction of this, as the qualitative form is sufficient for the applications which will be made of the principle.

339. Nitrous Acid. When nitrates, *e.g.* potassium nitrate, are treated with reducing substances, they lose oxygen and pass into the salts of another acid, known as *nitrous acid*. The new salts are called *nitrites*.

For this reduction, heating with metallic lead is generally employed. This acts according to the equation

$$KNO_3 + Pb = KNO_2 + PbO.$$
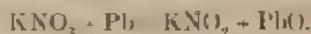
By extracting with water, the readily soluble potassium nitrite can be separated from the difficultly soluble lead oxide. Small quantities of lead which pass into solution by reason of a side-reaction, are precipitated by passing in carbon dioxide.

On attempting to liberate the acid HNO_2 from the salt, it is found not to be stable in the free state. On pouring sulphuric acid over potassium nitrite, brown vapours are formed which, indeed, have the composition of an anhydride of nitrous acid, N_2O_3, but which prove to be a mixture of nitric oxide and nitrogen peroxide. If these vapours be passed into water, a feebly blue coloured solution is obtained, which contains some nitrous acid, but which constantly evolves nitric oxide and passes finally into nitric acid in accordance with the equation $3HNO_2 = 2NO + HNO_3 + H_2O$.

The same vapours are also obtained when nitric acid is decomposed with reducing agents under certain conditions. On heating nitric acid of density 1·30 – 1·35 with arsenic trioxide (p. 50), the latter takes up one combining weight of oxygen from the nitric acid, and the nitrous acid formed breaks up into water and the brown vapours mentioned. Since the latter are used in many important chemical reactions, especially in organic chemistry, this method of preparation is often used.

If these vapours are cooled in a freezing mixture, a liquid of a blue to green colour is obtained, and from this there can be separated by fractional distillation a portion of a dark blue colour, boiling at 35°, which, especially at low temperatures, appears pure blue. This has the composition of nitrogen trioxide or nitrous acid anhydride, and can be regarded as the compound N_2O_3.

For the *detection of nitrous* NO_2' the general reaction for oxygen compounds of nitrogen by means of ferrous sulphate (p. 326), is, in the

...ee employed. It is distinguished from the ion NO_3' of nitric
...y the fact that even on acidifying the salts of nitrous acid, or
...trites, with any other stronger acids, the brown vapours are
...d the nature of which has just been given. By means of strong
...ng agents, NO_2 can be converted into NO_3'. A volumetric
...d depending on this will be given later on, under potassium
...ganate

...rther, nitrosion unites with cobalt (p. 55) to form "complex"
...ome of which are readily recognised. This reaction, however,
...s more used for the detection of cobalt than of nitrous acid, and
...erefore be described under that metal.
... heat of formation of nitrous acid in dilute aqueous solution
... elements is − 28 kj, in accordance with the equation H_2 + N_2 +
...q. − $2HNO_2$ aq.   2 − 28 kj.

Hyponitrous Acid.—By suitably regulating the reduction
...nitrates, a further amount of oxygen can be removed from them,
... *hyponitrites*, or the salts of *hyponitrous acid*, are obtained. Of
...ferent methods of their preparation, the most easily understood,
...cally, is that by means of sodium. This metal is dissolved in
...ry, and a solution of sodium nitrate or nitrite is treated with the
...m amalgam" so obtained. Sodium amalgam acts much more
...ately on other substances than pure sodium does, and is, there-
...etter adapted than the latter for many preparations. The
...n can be formulated as follows: -

$$2NaNO_3 + 8Na + 4H_2O = Na_2N_2O_2 + 8NaOH,$$
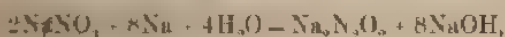
...odium nitrate is used, and

$$2NaNO_2 + 4Na + 2H_2O = Na_2N_2O_2 + 4NaOH,$$

...odium nitrite is employed.
...om the sodium salt, the difficultly soluble silver salt is prepared
...urified by washing. On decomposing this salt with hydrogen
...e with exclusion of water, by using ether (an organic com-
...) as solvent, hyponitrous acid, $H_2N_2O_2$, is obtained in the form
...te crystalline laminae, which are very unstable and explode
... The substance dissolves in water and yields a solution which
...rather longer, but which has also only a passing existence. It
...volves a gas having the composition N_2O, which is the anhydride
...onitrous acid.
...e same substance, N_2O, which bears the name *nitrous oxide*, is
...ed in many cases in which hyponitrous acid ought really to be
...   It is very much more stable than the latter, and it has not
...en found possible to convert it back into hyponitrous acid or
... its salts
...rous oxide is *usually prepared* by heating ammonium nitrate

With regard to this reaction, the reader is referred to the following section on the ammonia compounds ; we shall here give the properties of the substance.

Nitrous oxide is a gas consisting of two combining weights of nitrogen to one of oxygen, to which, in accordance with the density, the formula N_2O has to be ascribed. It is colourless, has a faint sweetish odour, and dissolves in water to a fairly large extent. At room temperature water absorbs about an equal volume of the gas. Likewise, the gas is comparatively easily liquefied, since its critical temperature lies at + 39 ; the critical pressure amounts to 78 atm. At 0 the vapour pressure amounts to 36 atm., and the vapour pressure of one atmosphere is found at – 90 , which is, therefore, the ordinary boiling point.

Nitrous oxide parts with its oxygen still more readily than nitric oxide, so that not only phosphorus and brightly burning wood continue to burn in it, but also charcoal and sulphur, if previously sufficiently heated. Sulphur burning with a small flame, however, is extinguished when introduced into the gas.

Nitrous oxide is taken up by the blood and causes unconsciousness ; it is therefore employed for obtaining transient narcosis. The gas cannot be decomposed by the organism in such a way that its oxygen becomes available ; if, therefore, nitrous oxide has to be inhaled for a lengthened period, it must be mixed with oxygen in the same proportions as the latter is present in the air.

In order to be formed from its elements, nitrous oxide would require to take up a large amount of energy, viz. $75 \, k_j$: $2N_2 + O_2$ $2N_2O$ $2 \times 75 \, k_j$ In its decomposition, the same amount of energy is given out in the form of heat.

341 Nitro-compounds. The acid actions of nitric acid depend on the fact that hydrion very readily splits off from the compound HNO_3. In view of the fact that other oxyacids, *e.g.* sulphuric acid, also give reactions in which *hydroxyl* acts in the place of hydrogen, the question must be asked whether, in the case of nitric acid, oxygen and hydrogen also act in common as hydroxyl.

From the fact of the strong electrolytic dissociation of nitric acid it can, in the first place, be presumed that if such reactions are to occur, one will expect them to do so in the *absence of water* (which, of course, causes the formation of hydrion). This is, in fact, found to be the case.

In organic chemistry, a large number of compounds are known which are formed by the action of nitric acid on compounds containing hydrogen ; the hydrogen from these, along with the hydroxyl from nitric acid, is eliminated as water, and the residual group NO_2 of the nitric acid unites with the residue of the organic substance, containing one combining weight less of hydrogen. The group NO_2 is called the *nitro group*, and the compound RNO_2 formed in accordance with this

reaction equation $RH + HNO_3 = RNO_2 + H_2O$, is called a *nitro*

In external appearance this process looks exactly like that of
mation of a salt, especially if the hydroxyl is assumed to be
as such in the nitric acid, and the equation, therefore, be
in the form $NO_2OH + HR = R . NO_2 + H_2O$. It would,
lead to mistakes if one were to estimate the significance of
parent agreement so highly as to regard both reactions as
lly the same. For, the nitric acid would then have to be
as the base, and the hydrogen compound RH as the acid, in
tion

The essential difference as compared with an ordinary salt forma-
ists just in the fact that we are in this case not dealing with
reaction as in the formation of a salt, for, neither is the com-
RH an acid, nor the nitric acid a base, nor, finally, the nitro-
formed a salt. According to what was said above, also,
erence becomes especially evident from the fact that the forma-
nitro-compounds takes place all the more readily the more
ely water is *excluded*, both the water originally present and
duced by the reaction itself. The latter can be rendered
by adding desiccating agents; and, as such, concentrated
acid is ordinarily employed. Nitration, or the preparation
ro-compound, is, therefore, usually carried out in the presence
or smaller amounts of concentrated sulphuric acid

o compounds can be formed not only from nitric acid, with
on of hydroxyl, but also from *nitrous* acid, with elimination of
In order that such an elimination may take place, there
present in the substance which is to pass into the nitro-com-
a part which will form a stable compound with the hydrogen
cases this will be hydroxyl, which will give water with the
en. We have then the equation

$$R . OH + HNO_2 = R . NO_2 + H_2O.$$
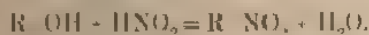
This equation has also only an apparent and no real resemblance
lt formation. This is most clearly seen from the opposite rôle
by the groups NO_2 and R.

tly, nitro-compounds can be formed by the action of *nitrogen*
on such substances as can directly form compounds by
on. The reaction corresponds to the formation of chlorides by
on of chlorine on substances of this class, *e.g.*, metals.

hereas, in organic chemistry, numerous nitro-compounds are
, the number of inorganic nitro compounds is comparatively
. Nevertheless, some of them are of sufficient importance to be
here

Nitrosulphonic Acid. — The most important inorganic nitro-

compound is nitrosulphonic or nitrosylsulphuric acid, the composition and reactions of which are expressed by the formula $SO_2\genfrac{}{}{0pt}{}{OH}{NO_2}$.

In order to obtain such a compound, one must act on the hydrogen compound of the radical $SO_2(OH)$ with nitric acid, or on the hydrogen compound of the same radical with nitrous acid. Both methods give the desired result.

The hydrogen compound of $SO_2(OH)$ is no other than sulphurous acid (p. 282); nitrosulphonic acid would, therefore, be formed from sulphurous acid and nitric acid.

As a matter of fact, this compound is obtained when, in place of sulphurous acid, its anhydride, sulphur dioxide, SO_2, is passed into concentrated nitric acid. This method has the especial advantage that no water is formed in the reaction, and the disturbances due to it are, therefore, not to be feared. The reaction takes place simply according to the equation $HNO_3 + SO_2 = SO_2\genfrac{}{}{0pt}{}{OH}{NO_2}$.

The object is also attained by the other method. If nitrous acid (or its vapours, which have the same composition as it, p. 332) be introduced into the hydroxyl compound of the radical $SO_2(OH)_2$, i.e. into concentrated sulphuric acid, nitrosulphonic acid is formed along with water; the latter is taken up by the excess of sulphuric acid. The equation of this reaction is $SO_2(OH)_2 + HNO_2 = SO_2\genfrac{}{}{0pt}{}{OH}{NO_2} + H_2O$.

Besides these two typical methods, there are a number of others which can in principle be traced back to them. Some of these methods will be mentioned later.

Nitrosulphonic acid is a white, solid, crystalline substance, which melts, with decomposition, at 73. It is very sensitive to water, and is transformed by it into sulphuric acid and nitrous acid (which, in turn, partially undergoes further decomposition, p. 332)—$SO_2(OH)NO_2 + H_2O = H_2SO_4 + HNO_2$. It dissolves, however, in concentrated sulphuric acid, and forms a very stable solution, which stands being diluted to some extent with water, corresponding equilibria being thereby established.

The compound also bears the name *leaden-chamber crystals*, for it is readily formed under the conditions prevailing in the lead chambers in the preparation of sulphuric acid, when too little water is present. By the addition of more steam, the leaden-chamber crystals, which are not formed in the well-regulated process, can easily be made to disappear.

Further, the retention of the valuable oxides of nitrogen in the waste gases from the sulphuric acid manufacture, which is effected by treating them with concentrated sulphuric acid in the "Gay Lussac tower" (p. 289), depends on the formation of nitrosulphonic acid under these conditions. On mixing the solution of nitrosulphonic acid in

Further, heated platinum catalytically promotes the combustion of ammonia. If a heated spiral of platinum wire is hung in a mixture of oxygen (or air) and ammonia, it continues to glow, and fumes of ammonium nitrate and nitrite are formed. If a mixture of ammonia and excess of air is rapidly passed over heated platinum foil, covered with a thin layer of spongy platinum, the whole of the ammonia can be oxidised to nitric acid.

Of the ammonium salts, that of nitric and of nitrous acid are of special importance here. The former yields large crystals which very readily dissolve in water, thereby producing a considerable lowering of temperature. If placed on glowing charcoal, it detonates, and when carefully heated decomposes smoothly into water and *nitrous oxide*—

$$NH_4NO_3 = N_2O + 2H_2O.$$

This is the most convenient and usual method of preparing nitrous oxide (p. 333).

Ammonium nitrite decomposes in a similar way, only much more easily—

$$NH_4NO_2 = N_2 + 2H_2O.$$

That is to say, water and nitrogen are formed. The reaction takes place very readily; it proceeds energetically even below the boiling point of water.

For this purpose it is not necessary to first prepare pure ammonium nitrite, but it is sufficient to bring the ions NH_4 and NO_2 together, i.e. it is sufficient, in order to obtain a regular current of nitrogen, to warm a soluble nitrite (e.g. commercial sodium nitrite) with an ammonium salt (e.g. ammonium sulphate) in aqueous solution.

It has been asserted that the reverse reaction, the combination of free nitrogen with water to form ammonium nitrite, also occurs, especially in the evaporation of water in the air. It must, generally speaking, it is true, be conceded that every chemical process which takes place in a definite direction also takes place in the reverse sense; in all cases it is only a question of *how much* is formed. Although exact determinations have not been made, it may be estimated that the formation of ammonium nitrite from nitrogen and water will most probably ensue only to an exceedingly *slight* degree, so that it seems very doubtful whether it will be possible to detect the amount formed, or indeed, whether the ammonium nitrite which may be found has been formed in this way.

349 **Amido-compounds.** When potassium is warmed in ammonia gas, it is converted into a white mass, which when fused appears blue; hydrogen is evolved in the process. This mass has the composition KNH_2, and is formed in accordance with the reaction
$$2K + 2NH_3 = 2KNH_2 + H_2.$$

Just as in the case of hydrogen chloride, HCl, and of water, H O, one combining weight of hydrogen can be replaced by potassium (or another metal), so, also, it is possible in the case of ammonia, H N. This replacement, however, becomes gradually more difficult. Whereas most of the metals can displace hydrogen from hydrochloric acid, only a few can do so in the case of water; and in the case of ammonia only the alkali metals have this power. The resulting product, also, is rather unstable : on being fairly strongly heated, it decomposes, and in contact with water it is converted into potassium hydroxide and ammonia, in a manner similar to the conversion of a metallic hydroxide into a metallic chloride and water, in contact with hydrochloric acid.

The residue, NH₂, produced by the loss of one combining weight of hydrogen from ammonia, has, in many compounds, a similar signif-cance to the residue of water, hydroxyl. It bears the name *amido*; so that the compound KNH₂ is called *potassamide*, and it is found in many compound substances. Since it is formed from ammonia by the loss of one hydrogen, it is *monovalent* and can take the place of hydrogen, chlorine, or hydroxyl. The amido-compounds are most readily obtained from (comparatively unstable) chlorine compounds, by acting on these with ammonia. The chlorine is then eliminated along with hydrogen as hydrogen chloride, which mostly combines immedi-ately with more ammonia to form ammonium chloride, and the amido residue takes the place of chlorine

$$R . Cl + 2NH_3 = R . NH_2 + NH_4Cl$$
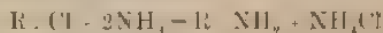
Another method of obtaining amido-compounds consists in the action of ammonia on hydroxyl compounds : $R . OH + NH_3 = R . NH_2 + H_2O$. As a rule, the action takes place only at comparatively high temperatures.

Thus, for example, *sulphamide*, generally called shortly *sulph-amide*, is obtained by the action of ammonia on sulphuryl chloride, $SO_2Cl_2 + 4NH_3 = SO_2(NH_2)_2 + 2NH_4Cl$. To ensure that the tempera-ture does not rise too high, the sulphuryl chloride is dissolved in a suitable solvent, and the ammonia is passed slowly in.

Sulphamide is a colourless, crystalline compound, which readily dissolves in water, and no longer exhibits the acid properties of sulphuric acid. Also, the solution does not appreciably conduct the electric current, since the substance is not a salt

On keeping the aqueous solution, the conductivity slowly increases, which shows that a salt is formed This occurs by the taking up of water : $SO_2(NH_2)_2 + 2H_2O = (NH_4)_2SO_4$. That is, ammonium sulphate is formed

This reaction is a general one. By the action of water, the amido-compounds pass into hydroxyl compounds plus ammonia. This is the reversal of the method of preparation of the amido-compounds given above ; the reversal takes place on the basis of the law of mass action

oxide. The latter substance has already shown itself a very
active and important accelerator in the manufacture of sulphuric
, i.e. in the oxidation of sulphurous acid by free oxygen (p. 289),
a number of other cases are also known in which it acts as an
erator of oxidation

In those cases, therefore, where it is desired to increase the oxidising
on as much as possible, *red, fuming nitric acid, i.e.* an acid which
tains lower oxides, especially nitrogen peroxide, in solution, is used.
acid is obtained by distilling nitric acid at a high temperature
321), or, also, by adding a small quantity of a reducing substance
ganic substance) during the distillation

Conversely, in those cases where we are dealing with other actions
nitric acid in which oxidation has to be *avoided*, acid as free as
sible from lower oxides must be used. This is recognised by its
g colourless, and the lower oxides, which are more volatile than
nitric acid, can be removed from the yellow acid by passing a
am of dry air through it. This is of importance, for example, in
preparation of nitro compounds from organic substances (p. 334)

**346 The Rôle of the Oxides of Nitrogen in the Preparation
Sulphuric Acid. Transfer Catalysis.** — Recent researches
ble us to form a somewhat more definite idea regarding the
eleration of the formation of sulphuric acid in the leaden chamber
ough the presence of oxides of nitrogen (p. 289). As the result of
eriment it has been found that whereas the *direct* oxidation of
phurous acid by free oxygen takes place with great slowness, both
formation of the nitro-compounds of sulphuric acid and of similar
stances from the above constituents in the presence of oxides of
ogen, and the decomposition of these compounds by excess of
er, take place with great rapidity. The increase in the velocity of
mation of sulphuric acid by the oxides of nitrogen can therefore be
lained by the assumption of such *intermediate reactions.* It has,
ever, not been definitely determined what the intermediate
stances are in the present case, since there are quite a number of
ducts having a composition intermediate between sulphurous acid
nitrous acid, all of which have the property of rapid formation
decomposition. It is therefore probable that there is not only
single intermediate substance produced, but that various inter-
iate compounds are formed and decomposed, the relative amounts
hese depending on the temperature, the amount of water, and the
centration of the substances involved.

Since these intermediate products undergo decomposition under
same conditions as those in which they are formed, we obtain th
ntial criterion of the catalytic processes, viz., that the accelerating
stance does not appear in the end product, and does not, therefore
d in any stoichiometric relationship to the amount of the latter
r such unstable intermediate forms can be produced at all depends

in so many cases that it constitutes one of the most important aids to the progress of science towards the knowledge of new compounds.
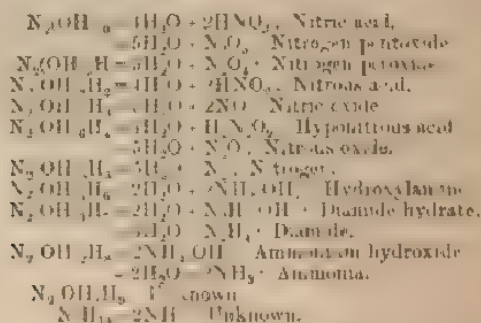
The substances we have mentioned do not complete the list of the nitrogen derivatives of sulphuric acid, but we must here forego the discussion of further details.

* In the same way as sulphuric acid, many other hydroxyl compounds can also yield amides and similar derivatives. Thus, for example, there is an amide of nitric acid, NO_2NH_2, obtained by a method which cannot here be discussed; it forms a white, crystalline mass, which at 70 rapidly decomposes into water and nitrous oxide. On account of this decomposability, it cannot be obtained by heating ammonium nitrate, whereas, otherwise, heating the ammonium salts constitutes a fairly general method for obtaining the acid amides.

350. **Other Oxygen-Hydrogen Compounds of Nitrogen.** — Besides the compounds of nitrogen already described, there are a number of others which contain both hydrogen and oxygen. The following list gives a review of the entire series of these compounds.

The highest stage of oxidation of nitrogen, viz., nitric acid, can be formally regarded, by the addition of $2H_2O$, as a compound of nitrogen with five hydroxyl groups: $HNO_3 + 2H_2O = N(OH)_5$. Doubling this formula in order to obtain an expression for the nitrogen compounds with $2N$, the following series is obtained by the gradual replacement of the hydroxyl groups by hydrogen:—

$$N_2OH_{10} = 4H_2O + 2HNO_3, \text{ Nitric acid,}$$
$$= 5H_2O + N_2O_5, \text{ Nitrogen pentoxide.}$$
$$N_2(OH)_8H_2 = 5H_2O + N_2O_4, \text{ Nitrogen peroxide.}$$
$$N_2OH_6H_2 = 4H_2O + 2HNO_2, \text{ Nitrous acid.}$$
$$N_2OH_6H_4 = 4H_2O + 2NO, \text{ Nitric oxide.}$$
$$N_2OH_6H_4 = 3H_2O + H_2N_2O_2, \text{ Hyponitrous acid.}$$
$$= 3H_2O + N_2O, \text{ Nitrous oxide.}$$
$$N_2OH_4H_6 = 5H_2 + N_2, \text{ Nitrogen.}$$
$$N_2OH_4H_6 = 2H_2O + NH_2OH, \text{ Hydroxylamine.}$$
$$N_2OH_2H_8 = 2H_2O + N_2H_4OH + \text{ Diamide hydrate.}$$
$$= 4H_2O + N_2H_4, \text{ Diamide.}$$
$$N_2OH_2H_8 = 2NH_2OH, \text{ Ammonium hydroxide.}$$
$$= 2H_2O + 2NH_3, \text{ Ammonia.}$$
$$N_2OH_{10} \text{ Unknown}$$
$$NH_{10} = 2NH_5, \text{ Unknown.}$$

According to this table, ammonia appears as the last known member of the series of reduction compounds of nitric acid, and between it and nitrogen, which stands in the middle, two stages are present which are known, and to which the names *hydroxylamine* and *diamide* (or *hydrazine*) have been given.

Hydroxylamine, NH_3O, is formed under various conditions by the reduction of nitric acid or other oxygen compounds of nitrogen. It is obtained chiefly in the form of a hydrochloride, from which the pure compound can be obtained by decomposition with a base, with exclu-

...., the whole amount of gas can ultimately be made to combine. ....urs, for example, when the gases are kept in contact with an ... Ammonia is taken up by acids, and if sparks are continued to ...ed through the gas mixture while standing over an acid, all the ... ... ultimately disappear.

As is apparent from the equation

$$N_2 + 3H_2 = 2NH_3,$$

... volume diminishes from 4 to 2, or to a half, when the elements ... into combination. The reverse change takes place when the gas ... .posed.

The change of energy occurring in the process is represented by ... equation $N_2 + 3H_2 = 2NH_3 + 2 \cdot 50$ *kj.*

Ammonia is absorbed in large amount by water, viz., about 800 ...mes, or 0·6 part by weight, at room temperature. It, however, ...ows Henry's law to some extent, especially at higher tempera ... It can be completely removed from the solution by boiling. ... this it is apparent that all solutions of ammonia must necessarily ... a lower boiling point than pure water. For if there were a ... ... with higher boiling point, this would remain behind during ... ...tillation, and finally pass over unchanged in composition.

The aqueous solution of ammonia colours red litmus paper blue, ... therefore contains hydroxidion, OH'. It must be concluded, ...fore, that in water ammonia has passed, at least partially, into ... ...pound containing hydroxyl. This can occur only by it taking ...he elements of water, and, therefore, a compound of the general ... ...th $NH_3 \cdot nH_2O$ is present. All known facts favour the view ... ., and that the compound must, therefore, be written ... $\cdot H_2O$, or, giving prominence to hydroxyl, NH_4OH.

Just as we recognised the compound ion of nitric acid, NO_3', to be ... ...ar to the simple ion Cl' of hydrochloric acid, we also conclude ... in the solution of ammonia there is present along with hydroxyl ... compound cation NH_4, which corresponds to sodion, Na'. Since ... ... combined with only one hydroxyl, it is monovalent, like ... ...ion or sodion. In other respects, also, *e.g.* in the crystalline ... ... corresponding saline compounds, the ion NH_4', or *ammonion*, is ... similar to potassium.

Ammonia must, therefore, be regarded as the *anhydride* of ... ...ium hydroxide, NH_4OH. It has not as yet been possible to ... ...pare ammonium hydroxide in the pure state, just as only the ... ...oxide of sulphurous acid, SO_2, and not sulphurous acid itself, ... SO_3, is known. As to its existence, however, or rather as to the ... ...ence of the ion NH_4' or ammonion, no more doubt exists than ... ... the existence of the ion of sulphurous acid, SO_3''.

This assurance is based chiefly on the fact that there are a large ... ...mber of salts which can be prepared from ammonia and acids, and

The substance has received the name *hydrazine* (from *azote* = nitrogen); it is also called diamide, since the atomic group NH_2 has long been called amide.

Hydrazine is a colourless liquid which boils at 114° and solidifies at 1°. It combines with water to form a hydrate N_2H_4O, which is volatile without decomposition. In a further quantity of water it dissolves, yielding a liquid with an alkaline reaction, from which the salts of hydrazine can be obtained by neutralisation with acids.

Two series of such salts are known, monacid and diacid. The former have the composition $N_2H_4 . A$, the latter, $N_2H_4 . A_2$. The corresponding hydroxides are, therefore, $N_2H_4(OH)$ and $N_2H_4(OH)_2$.

The salts of the second series are, however, very unstable and readily decompose into salts of the first series and free acid. In aqueous solution, the same decomposition takes place almost completely. The aqueous solution, therefore, even of the free base, consists essentially of $N_2H_4(OH)$ and of the ions of this monacid base, viz. N_2H_5' and OH'. The ions formed from this by accession of water, N_2H_6'' and $2OH'$, are present to quite a small extent.

The solutions of hydrazine have a powerfully reducing action, and exceed in this respect even the hydroxylamine solutions.

352. Hydrazoic Acid.— The last compound of this series which we shall mention here is hydrazoic acid, HN_3. It did not find a place in the general summary given on p. 348, since it contains three combining weights of nitrogen, and that list was extended only to two combining weights of that element.

Hydrazoic acid was first obtained by the decomposition of organic compounds of complex composition; not until later was a method discovered for preparing it from simpler substances. One of the simplest methods of preparation is from hydrazine and nitrous acid in aqueous solution. There occurs the reaction $N_2H_4 + HNO_2 = HN_3 + 2H_2O$. Further, the sodium salt of hydrazoic acid, NaN_3, is obtained by passing nitrous oxide over heated sodamide (p. 346). The reaction is $NH_2Na + N_2O = NaN_3 + H_2O$. The acid can be obtained from the sodium salt by distillation of the aqueous solution after the addition of sulphuric acid.

On distilling the aqueous solution obtained by one or other method, the acid first passes over and can in this way, finally also by the use of dehydrating agents, be obtained in the pure state. Hydrazoic acid is thus obtained as a colourless liquid with a strong and very unpleasant smell, which boils at 37°, and explodes very readily with great violence. The same property is also possessed by many of its salts in the solid state. In solution, however, the acid is fairly stable.

In the case of this compound, the acid properties are clearly although not very strongly developed; a 1 per cent aqueous solution is dissociated to the extent 0·008 into its ions. On account of the slight dissociation, it can be separated from its aqueous solutions by

If the water is *removed*, the amide can be formed from the hydroxyl compound and ammonia ; if, conversely, *excess of water* is present, it converts the amido-compound into the hydroxyl compound

The question may be asked if an intermediate stage does not exist between the sulphamide and the ammonium sulphate, just as chloro-sulphonic acid is an intermediate stage between sulphuryl chloride and sulphuric acid. As a matter of fact, such a compound exists. From chlorosulphonic acid and ammonia, there is formed *sulphamine acid*—

$$SO_2ClOH + 2NH_3 = SO_2{NH_2 \atop OH} + NH_4Cl.$$
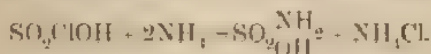
In harmony with the fact that acid hydrogen is still present, *sulphamine acid* or *amidosulphuric acid* is a monovalent acid. It is a colourless substance which crystallises well and readily dissolves in water with an acid reaction ; the solution is, however, a weaker acid than sulphuric acid. This is a general phenomenon ; the entrance of an amido group reduces the acid properties.
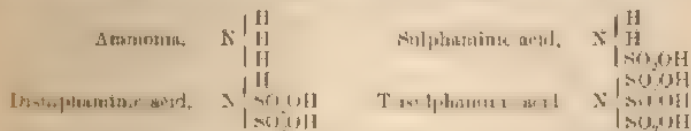
Sulphamminarium is produced in the form of its ammonium salt by the gradual action of water on the dissolved sulphamide

$$SO_2(NH_2)_2 + H_2O = NH_4SO_3 . NH_2.$$
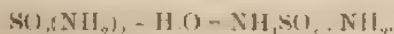
By this reaction, sulphaminic acid shows itself still more clearly as an intermediate compound between sulphamide and sulphuric acid.

Sulphaminic acid is also produced by a number of other reactions, some of which will be discussed later.

Sulphaminic acid can also be regarded as a derivative of *ammonia*, which has been formed by one hydrogen of the latter being eliminated as water with one hydroxyl of the sulphuric acid, the two residues NH_2 and HSO_3 then uniting together. The question may be asked if the same reaction may not occur more than once with ammonia, so that two or three of its hydrogens experience the same substitution. Such is the case, the following substances being known

Ammonia,	$N \begin{cases} H \\ H \\ H \end{cases}$	Sulphamine acid,	$N \begin{cases} H \\ H \\ SO_3OH \end{cases}$	
Disulphamine acid,	$N \begin{cases} H \\ SO_3OH \\ SO_3OH \end{cases}$	Trisulphamine acid	$N \begin{cases} SO_3OH \\ SO_3OH \\ SO_3OH \end{cases}$	

Into the preparation and properties of these substances we shall not enter here ; rather they have been mentioned only for the purpose of showing how conclusions by analogy may furnish a clue in searching for new substances, the possibility of *one* definite re   on giving rise to the presumption that similar reactions are po Such conclusions do not always lead to a positive result, since ci stances may exist which show that the analogy in question do hold, or that it is impracticable. Still the method has proved

CHAPTER XV

PHOSPHORUS

354. General. —The name *phosphorus* (light-bearer) was formerly used to designate all substances which possess the property of emitting light without at the same time having a correspondingly high temperature. The name phosphorescence, used in physics for the after luminescence shown by certain substances after a previous exposure to light, is a relic of that usage. At the present day, the name phosphorus is confined to one element, which also exhibits the above property of cold luminescence, although for a different reason.

Phosphorus was discovered about the year 1670 by an alchemist Brandt, who obtained it by the distillation of the residue left on the evaporation of human urine. He kept his method secret, but it was soon found out by Kunkel in Germany, and Boyle in England. Gahn and Scheele also soon found that the bones of the vertebrate animals were a much richer source of phosphorus, and at the present day it is still chiefly prepared from these.

The method of obtaining phosphorus depends on the fact that the oxygen compound of phosphorus, phosphoric acid, which is contained in the bones, is reduced by charcoal. The charcoal combines with the oxygen, and the phosphorus is set free and distils over. The reaction cannot be given here in detail, but will be more fully described later (Chap. XXIII.)

In nature, phosphorus occurs only in the form of salts of the just mentioned phosphoric acid. These compounds are very wide-spread although they do not occur anywhere in large quantities. They are of great importance for organic life, since the "protoplasm" of the cell, the substance to which the actual vital activity is attached, always contains small amounts of phosphorus compounds. The nerve and brain substances, more especially, are comparatively rich in phosphorus, which is there present in the form of phosphoric acid derivatives.

Salts of phosphoric acid or the phosphates are also indispensable for the growth of plants. As the soil does not usually contain much of it, this substance is, for the purpose of high cultivation, added to the soil

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...menon.   Many other gases, especially the vapours of organic ...es, such as oil of turpentine or alcohol, behave differently; ...vent the luminescence, even when they are present in very ...mount   The reason is a great retardation of the velocity of ... between phosphorus and oxygen; the phenomenon is, there-...atalytic one.   This behaviour is of importance for the above-...ed method of detecting phosphorus by means of the lumin-...since it can make it appear as if phosphorus were absent when, ... it is present.

...(SO) is formed in the slow combustion of phosphorus in ...air, and can be readily recognised by its smell; that which is ...termed phosphorus smell is nothing but the smell of ozone. ...vapour of phosphorus itself has a smell like garlic. One can ...of oneself of this by preventing the destruction of the vapour ...ing traces of a substance which prevents the slow oxidation. ...ean stick of phosphorus, half covered with water, is allowed to ...in a large flask, whereby it is advantageous to slightly raise ...erature, the air of the flask soon becomes full of ozone, and ...ions of this substance given on p. 80, especially the turning ...of potassium iodide and the bleaching of litmus, can be easily ...strated

...ce ozone is a substance which is formed from oxygen by the ...gain of free energy, this energy must come from somewhere ...Evidently it is the oxidation of the phosphorus which yields ...energy   In accordance with the principle stated on p. 206, such ...cess can be brought about only by a *coupled* reaction, and it must, ...fore, be concluded that the formation of ozone takes place in such ...way that the ratio of the amount of oxidised phosphorus to that of ...ozone produced is definite and a whole number. This is, indeed, ...case   the experiments made on this point have shown that equal ...nts of oxygen are used up for the oxidation of phosphorus and ...the formation of ozone. It has, however, not yet been established ...at the chemical reaction here is.

... **Phosphorus Vapour.**—The combining weight of phosphorus ...found, from its chemical relations, to be 31 : the molar weight of ...vapour, calculated from its vapour density, has been found, how-...er, equal to 124, so that to this vapour the formula P_4 must be ...ibed   In this respect, therefore, phosphorus differs essentially ...m nitrogen, to which it exhibits many points of resemblance in ...case of its compounds, and is related to sulphur.

...very high temperatures, the density of phosphorus vapour ...mes less   Exact measurements of the progress of this process, ...h presumably consists in the transformation into P_2, are not ...wn.

...In accordance with the relations existing between white and red ...osphorus, as described on p. 354, the two forms have a very different

onsists are found, on microscopic examination, ea
ight, to be crystalline.   The conversion of white
is accompanied by an evolution of heat equal to 1

356. **Reciprocal Transformation of the tv**
phorus.—That red phosphorus is formed from
has already been mentioned.   The velocity of t
very greatly on the temperature : at 300° it is
however, it is very great—so great, indeed, th
takes place.   For, since a considerable amount
in the transformation, the temperature of the
spontaneously, and the velocity of transformatio
so increased that a portion of the phosphorus o
the heat produced.

The velocity of transformation can be very
means of catalytically acting substances, so that t
formation even at a low temperature is consideri
tically accelerating agent has been found in *ww*
even when present in very small amount.   Li
divided product, which consequently has a brigh
obtained from a solution of yellow phosphorus
bromide (p. 363) at 170°.

Light exercises a similar, accelerating influe
phosphorus which have been kept for some
glass bottle, become covered with a red layer w
of red phosphorus.   In such a case, it can g
that the outside parts, which have been most
light, are correspondingly darker in colour.

Although such different conditions are ki
phosphorus passes into red, there is only one
reverse transformation.   It consists in c
phorus into vapour and quickly cooling tl
condenses then to colourless liquid or solid

If these facts are examined in the light
we have seen to exist between polymorph
case of sulphur (p. 258), we must regard t'
unstable form compared with the red.   Th
various spontaneous transformations which
high temperatures, and under the influenc
although the latter circumstance is not
greater solubility of white phosphorus also

The formation of white phosphorus
case of the law that the *less stable* form ti

In the case of polymorphous sub
possibilities.   Either the two forms can
either side of which the relative stat
with sulphur (p. 258); or as in the

(p. 241), the one can be the stable, the other the unstable form, throughout the whole accessible range of temperature up to the melting point. Substances of the first kind are called *enantiotropic*, those of the second, *monotropic*. In the case of white and red phosphorus, is the relationship one of enantiotropy or of monotropy?

At fairly high temperatures, red phosphorus is certainly the more stable, since it is produced spontaneously from the white. At lower temperatures, the relationship is also the same, as is proved by the greater solubility of the white form. Consequently, phosphorus must be regarded as *monotropic*, and the red phosphorus is under all circumstances the more stable form compared with the white. It is also the more stable form with reference to *liquid* phosphorus, since, indeed, the conversion into red phosphorus at higher temperatures takes place from the liquid, because white phosphorus melts as low as 44°.

Objection could be taken to this view on the ground that white phosphorus can be kept for a very long time, even in contact with the red form, without transformation taking place. This, however, only proves that the velocity of transformation at room temperature is very small. This is not a mere assumption made to explain the present relations, but is seen to be in accordance with the rule when the following facts are kept in view.

As has already been mentioned several times, the velocity of chemical reaction increases with a rise of temperature in such a way that a rise of 10° or 15° corresponds to a doubling of the velocity, and the reverse holds for a lowering of temperature. Now, the transformation at 250 takes place in a few hours; assume it to occur in one hour, and assume, further, that a doubling of the velocity takes place only with every 15°, then the reaction at 10° lasts 2^16 hours, or about eight years. If we assume, however, that the velocity is doubled by a rise of 10°, then the time of transformation at 20° is found to be 1000 years. This rough calculation shows that the assumption of a very small velocity of transformation at room temperature contains nothing contradictory to the general laws.

357. The Oxidation of Phosphorus in Air. Not only does there attach to the slow combustion of phosphorus in the air the historical interest that it led, by reason of the peculiar emission of light, to the discovery of this element, but there still exist at the present day, questions of scientific interest with relation to this long-known phenomenon, which have not as yet received a satisfactory answer.

Phosphorus is luminous in the air at ordinary temperatu at the same time undergoes oxidation. The higher the temp rises, the more vigorous does this slow combustion become, pas about 45, into rapid combustion.

If the concentration of the oxygen is diminished, *e.g.* by al

phenomenon, since the hydrogen phosphide, in consequence of its ready decomposability, will always contain traces of phosphorus vapour.

If the spontaneously inflammable gas is kept some time, it loses the property of spontaneous inflammability, although analysis cannot detect any essential difference. It was, therefore, at first thought that two different kinds of hydrogen phosphide of the same composition existed, until it was found that the property of spontaneous inflammability belonged not to the pure hydrogen phosphide PH_3, but to another hydride of phosphorus having the composition P_2H_4, which is produced in small amount along with PH_3, and whose presence is the cause of the spontaneous inflammability

This can be proved by passing the spontaneously inflammable hydrogen phosphide through a freezing mixture. The less volatile spontaneously inflammable hydrogen phosphide separates out, and the issuing gas has now lost the property of igniting spontaneously.

The composition of hydrogen phosphide recalls that of ammonia, and in view of the manifold resemblance between nitrogen and phosphorus, basic properties will also be looked for in the case of hydrogen phosphide. As a matter of fact, these exist, but in exceedingly slight degree.

Hydrogen phosphide combines most readily with the halogen hydracids, above all with hydriodic acid. Both gases combine directly on being brought together, forming a crystalline mass which has the same crystalline form as ammonium chloride. Its composition is represented by the formula PH_4I, exactly corresponding to ammonium chloride, NH_4Cl. On attempting, however, to dissolve this white mass, which bears the name *phosphonium iodide* (phosphonium = PH_4) in water, hydrogen phosphide is evolved, and we are left with only a solution of hydriodic acid.

* In order to obtain phosphonium iodide, it is not necessary to prepare the two gases separately, but it can be obtained in one operation by the action of phosphorus and water on iodine For this purpose, white phosphorus (4 parts) is placed in a retort along with iodine (10 parts), and carefully heated with water (3 parts). A two-fold reaction takes place, one portion of the phosphorus withdrawing oxygen from the water, so that the hydrogen can combine with the iodine to hydrogen iodide. On the other hand, the hydrogen so produced goes to form hydrogen phosphide. The total reaction can be expressed by the equation $5I + 9P + 12H_2O = 4HPO_3 + 5PH_4I$.

The above mentioned hydrogen phosphide, which inflames spontaneously in the air, has the composition P_2H_4; it is a colourless liquid, which boils at 57 . It is an unstable substance, and in light as well as in contact with various catalytic substances it yields a yellow, solid substance, P_4H_2, or *solid hydrogen phosphide*, hydrogen phosphide gas being formed at the same time.

361 Halogen Compounds of Phosphorus —Phosphorus combines in several proportions with all the halogens, so that we have a large variety of different compounds. These are mostly very active, i.e. have a tendency to undergo decompositions with other substances, and are used as important reagents in many preparations.

If chlorine is passed over phosphorus contained in a retort from which the air has been previously displaced by carbon dioxide, in order to prevent the phosphorus igniting spontaneously, direct combination of the two takes place. The heat thereby developed is sufficient to vaporise the greater part of the compound formed, and it condenses, therefore, in the receiver as a colourless liquid.

The reaction proceeds in the above manner when a sufficient amount of phosphorus is present; if, however, the chlorine is in excess, another substance is formed, which will be discussed later.

The above substance is obtained in the pure state by distillation, some phosphorus being added to retain any excess of chlorine which may be present. It forms a colourless liquid which boils at 76°, and has a density 1.6. The molar weight of the vapour is 138. According to this, and in accordance with the results of analysis, it has the formula PCl_3; it is called *phosphorus trichloride*, or, in view of the existence of a higher chloride of phosphorus, *phosphorous chloride*.

Phosphorus trichloride reacts readily with water and other substances containing hydrogen and oxygen. The reaction thereby proceeds in such a way that the chlorine combines partially or entirely with hydrogen to form hydrogen chloride, while the oxygen unites with the phosphorus to form an acid, phosphorous acid, which will be described later. In this way phosphorus trichloride acts as a dehydrating agent, and it is not necessary that the water should be present as such, but may be represented in the compounds merely by its elements. The reaction has nothing to do with the "predisposing affinity" (p. 365), for as the hydrogen and the oxygen here experience quite different fates, they need not have previously stood in any direct relation to one another.

The above mentioned decomposition is also brought about by the water vapour of the air, and for this reason phosphorus trichloride fumes when its vapour comes in contact with moist air.

In the formation of the trichloride, 316 kj are developed.

When chlorine is allowed to act on phosphorus or on the trichloride it is readily absorbed, and there is formed a solid substance of pale yellowish-green colour, which contains five combining weights of chlorine to one combining weight of phosphorus, and is therefore called *phosphorus pentachloride* or *phosphoric chloride*.

Phosphorus pentachloride, PCl_5, does not melt under the ordinary pressure, since its boiling point lies below its melting point. Since, however, the boiling point of all substances rapidly rises as the pressure increases, *whereas the melting point is affected to scarcely an appreci-*

able extent by pressure (p. 132), the boiling point ca
the pressure, be brought nearer and nearer to the mel
finally reach it.   In the case of phosphorus pentachlorid
ture is 148°, and the pressure amounts to severa
Under these circumstances, the pentachloride can simul
in the solid, liquid, and vaporous states, just as, e.g.,
(more exactly, at + 0·0073°, p. 134).   Under a still g
the pentachloride behaves like most other substances,
and afterwards boils if the temperature is further raise

In accordance with the formula PCl_5, the vapour
pentachloride should have the molar weight 208.   Th
of this, however, shows that this value is never reach
actual density of the vapour is less.   The differe
density being so much the less the higher the tem
lower the pressure.   In this respect, the vapour of
behaves in a perfectly similar manner to the va
peroxide (p. 327).

Here, also, it can be assumed that the vapour
stance, but that the pentachloride in the vapor
dissociates into phosphorus trichloride and chlorine
the equation $PCl_5 = PCl_3 + Cl_2$.   Such a mixture
chlorine must have half the density of the vapour
for, as the equation shows, one volume of the va
the same pressure into two volumes of its de
The observed values of the molar weight lie l
208 and 104, and from the densities observed u
the proportions of trichloride vapour and chlo
a mixture of that density can be calculated (p.

Confirmation of this view can be obtaine
The vapour of the pentachloride has the ye
chlorine only in a slight degree.   If, now, it
proportions chlorine must be mixed with any
to yield a gas of the same colour as the pent
be concluded that the same proportion of chl
The determination made in this way of the
vapour of the pentachloride agreed sufficient
from determinations of the density, on tl
dissociation into trichloride and chlorine.

Phosphorus pentachloride fumes stron
powerful irritant action on the mucous me
be exercised in working with it.   With
decomposition, with formation of phosph
(vide infra).   The pentachloride, also, act
similarly to the trichloride.   In this ca
large amount of chlorine contained in th
place comes into action, and the pentacl

·rt it
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re and
atively
i water
· hydro-

·rm three
of hydro-
·l salts and
·i numerals
Thus, mono-
·nosphate is
·', only salts

·nosphoric acid
·n is obtained.
·hich would be
to the equation
·quired to pro-
litmus appears
which the liquid
depends on the
·s the blue colour

in the dissociation
·sociation $H_3PO_4 =$
measurable amount.
·s place only in very
$= H^· + PO_4^{···}$, is ex-
·lt, e.g. the solution
·ting ion $PO_4^{···}$ cannot
sense of the equation
·roduced, and the liquid
·s, we have here again

·es in slight degree a
$IPO_4'' + H_2O = H_2PO_4' +$
·rgoes slight hydrolysis,
·tion. This is, however,
·alt.

·le by side, and ·
·ntion, it is clear
·y disappear, as in
·radually and contin.

phoric acid. When phosphoric acid is spoken of wi
*ortho*phosphoric acid is always meant.

Of the three acids, the last is by far the most
nature, compounds of it alone are found, and the
spontaneously, in aqueous solution, into the orthoph
as the different forms of sulphur at the ordinary t
ultimately into rhombic sulphur as being the most

Orthophosphoric acid is obtained by dissolvin
oxide in water and allowing the solution to stand
preferably in the heat. The least stable form, ma
first formed, and this gradually passes into the st
is obtained more conveniently by oxidising wl
dilute nitric acid. The phosphorus dissolves wi
oxide ; the phosphoric acid which is formed can
the excess of nitric acid and its reduction pro
centrating and heating.

Orthophosphoric acid is obtained in this w
which crystallises only slowly and with difficu
of the pure acid is 42 ; the melting point is
of water, and likewise, also, by the presence of
This is due to the general fact that the me
stance is lowered by the presence of a forei

Impure phosphoric acid is obtained fro
the mammals consist partly of the calcium
and partly of organic nitrogenous matter wl
passes into glue. If the bones are heated
black owing to the carbonisation of the
tinuing the heating, the charcoal burns a
left in the form of white masses retaini
bones. This residue is called *bone-ash*

If powdered bone-ash is mixed with
occurs a reaction of the kind described
is a difficultly soluble salt, and for this
sulphuric acid and calcium phosphate.
at the same time. On filtering the ma
phoric acid which is formed is separate
sulphate.

Since, however, this salt is not
amount of it remains in the soluti
pure calcium phosphate, and some
soluble compounds under the action
acid obtained in this way is not
many technical purposes.

As can be gathered from this de
in water. Indeed, it is so soluble
been determined. Even small an

...at of phosphoric acid below room temperature, and thus convert it ...a solution which, certainly, contains only a small quantity of the ...nt, i.e. of water.

The aqueous solution reacts acid to litmus, and has a pure and ...antly acid taste. Its electrical conductivity is comparatively ...: one mole of phosphoric acid dissolved in 10 litres of water ...tains only a quarter as much hydrion as an equally dilute hydro...ric acid solution.

Phosphoric acid is a *tribasic* acid and can therefore form three ...es of salts in which one, two, or three combining weights of hydro...are replaced by metals. Since there are two different acid salts and ...normal salt, these are distinguished by stating in Greek numerals ...many combining weights of hydrogen are replaced. Thus, *mono*...sium phosphate is the salt KH_2PO_4, *di*sodium phosphate is ...HPO_4, and *tri* silver phosphate is Ag_3PO_4. In nature, only salts ...last type, or normal salts, occur.

On attempting to neutralise an aqueous solution of phosphoric acid ...caustic soda with the aid of litmus, no sharp transition is obtained. ...ead of the three combining weights of caustic soda which would be ...ired for the formation of the normal salt according to the equation ...$PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$, less than two are required to pro...e an alkaline reaction, and the blue coloration of litmus appears ...ually, so that no definite moment can be given at which the liquid ...is neutral. Also, the amount of caustic soda depends on the ...on: the more dilute the solution, the sooner does the blue colour ...ear.

The cause of these phenomena is the difference in the dissociation ...the three hydrogens of phosphoric acid. The dissociation $H_3PO_4 =$ ...H_2PO_4, occurs comparatively easily and in measurable amount. ...further dissociation $H_2PO_4 = H^+ + HPO_4$, takes place only in very ...ght degree, and the third dissociation, $HPO_4 = H^+ + PO_4$, is ex...emely slight When, therefore, a normal salt, *e.g.* the solution ...Na_3PO_4, is dissolved in water, the corresponding ion PO_4, cannot ...st but acts on the water of the solvent in the sense of the equation ...$O_4 + H_2O = HPO_4 + OH$. Hydroxidion is produced, and the liquid ...st therefore, react alkaline. In other words, we have here again ...case of hydrolysis (p. 250).

...he divalent ion, HPO_4, also experiences in slight degree a ...milar transformation in aqueous solution, $HPO_4 + H_2O = H_2PO_4 +$ ...H, so that the disodium phosphate also undergoes slight hydrolysis, ...d therefore exhibits a feeble alkaline reaction. This is, however, ...ch feebler than in the case of the normal salt.

...Since these different equilibria exist side by side, and are also ...pendent on the temperature and the dilution, it is clear that on ...neutralisation the hydrion does not suddenly disappear, as in the case ...strong acids, *but its amount diminishes gradually and continuously*.

For this reason, no sudden but only a continuous change of c[o]
occurs when litmus is present.

The heat of formation of the trivalent phosphanion PO_4''', amo[unts]
to 1246 kj, that of the divalent hydrophosphanion, PO_4H'', 1277

366. **Pyrophosphoric Acid**.—If orthophosphoric acid is care[fully]
heated to 250°, it loses water and is converted into pyrophosph[oric]
acid, $H_4P_2O_7$. This process takes place in accordance with [the]
equation

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

A sure means of obtaining pure pyrophosphoric acid is to [heat]
such salts of orthophosphoric acid as contain just enough hydrog[en to]
yield a residue of pyrophosphate. This happens in the case of [the]
salts in which two hydrogens are replaced by metal, e.g. ordinar[y]
sodium phosphate. If this salt is heated, the following reaction t[akes]
place—

$$2HNa_2PO_4 = Na_4P_2O_7 + H_2O.$$
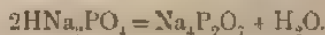
The free pyrophosphoric acid can be obtained in aqueous solu[tion]
from the pyrophosphate thus formed, by converting the latter into [the]
difficultly soluble lead salt and decomposing this with sulphur[etted]
hydrogen.

Unlike pyrosulphuric and pyrosulphurous acids (pp. 294 and 2[ ])
pyrophosphoric acid retains its state in aqueous solution for a t[ime]
and changes only slowly into orthophosphoric acid. The latter re[pre]-
sents the stable state to which the aqueous solution of the acid u[nder]
all circumstances approaches. The velocity with which this condi[tion]
of equilibrium is reached, depends on the temperature and the c[on]
centration of the hydrion in the solution; the latter accelerates [the]
transformation catalytically. For this reason, the transformat[ion]
takes place much more quickly if nitric acid is added to the solu[tion]
and the concentration of the hydrion thereby increased

Apart from the composition of the salts, pyrophosphanion is [dis]
tinguished by various reactions from orthophosphanion. A[s is]
apparent from the formula, it is tetrabasic, and forms, accordin[g to]
four series of salts. The neutral or normal salts contain two c[om]
bining weights of a monovalent metal or monovalent cation to [one]
combining weight of phosphorus, whereas normal salts of orthoph[os]
phanion contain three combining weights of a monovalent cation [to]
one of phosphorus.

To distinguish the two ions, silver nitrate is added to the so[lu]
tion. If the ion PO_4''', be present, a yellow silver salt of the comp[osi]
tion Ag_3PO_4 is precipitated; pyrophosphates, or the ion P_2O_7'''', gi[ve]
on the other hand, a white precipitate of the composition $Ag_4P[_2O_7]$
By means of this reaction also, one can observe the slow transforma[tion]
of a solution of pyrophosphoric into orthophosphoric acid.

367 Metaphosphoric Acid.—On heating orthophosphoric acid strongly, it passes into *metaphosphoric* acid, which analysis shows to the composition HPO_3. Its composition is, however, not represented by the simple formula but by a multiple formula $(HPO_3)_n$, where n whole number. There are various metaphosphoric acids which are distinguished from one another by the difference in the value the chemistry of these compounds, however, has as yet been up only to a rather small extent.

Metaphosphoric acid obtained in the above manner forms a glassmass which, at a moderately high temperature, melts to a viscous and, on cooling, forms an amorphous solid. The "glacial" acid of commerce is metaphosphoric acid. It dissolves in yielding an acid liquid whose reactions are different from those other phosphoric acids. It gives, indeed, like pyrophosphoric a white silver salt, but has the further property of *precipitating*, a property which is not possessed by the other phosphoric A solution of metaphosphoric acid is used, therefore, to detect presence of albumen, e.g. in urine. For this purpose, the solution acid must be freshly prepared since, on keeping, it is slowly converted into orthophosphoric acid.

For this transformation, the same general remarks hold as were for the corresponding transformation of pyrophosphoric acid. phosphoric acid has, however, not been detected as an intermediate although, on theoretical grounds, it is probable that it is formed.

Also when phosphorus pentoxide is dissolved in water, metaphosphoric acid is formed as the first product, and not the form which is stable under these circumstances, viz., orthophosphoric acid, in accordance with the general law of the first appearance of the less forms.

368. Chlorides of Phosphoric Acid.—If orthophosphoric acid capable of further taking up one combining weight of water, a acid would be produced: $H_3PO_4 \cdot H_2O = H_5PO_5$ or $P(OH)_5$. one can imagine all the hydroxyls of this acid to be replaced by we obtain PCl_5, the phosphorus pentachloride already described. As a matter of fact, the chloride, when decomposed with yields phosphoric acid along with hydrochloric acid: $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$.

Besides this chloride, there is also known the chloride of orthophosphoric acid, if the formula of this is written $PO(OH)_3$. This has the composition $POCl_3$, and is usually called phosphorus chloride.

Phosphorus oxychloride is a colourless liquid, which has the density and which boils at 107 and fumes in the air. It is violently decomposed by water to hydrochloric and orthophosphoric acids. $POCl_3 + 3H_2O = H_3PO_4 + 3HCl$.

2 B

The compound is prepared by the action of small amounts of water on the pentachloride $PCl_5 + H_2O = POCl_3 + 2HCl$. In place of water, numerous other compounds can be used in which oxygen and hydrogen are present. If such a compound is represented by the formula $R . OH$, the reaction takes place according to the equation $R . OH + PCl_5 = R . Cl + POCl_3 + HCl$. In the case of hydroxyl compounds, this reaction occurs so readily and regularly that it is used to determine whether hydroxyl should be assumed in any given compound or not. In organic chemistry, especially, phosphorus penta-chloride is used in this way as a reagent for hydroxyl.

As an example of this action, it may be cited that sulphuric acid, on being treated with phosphorus pentachloride, yields chlorosulphonic acid or sulphuryl chloride (p. 305), according to the proportions used. The reactions take place in accordance with the equations $SO_2(OH)_2 + PCl_5 = HOSO_2Cl + HCl + POCl_3$ and $SO_2(OH)_2 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl$.

Similarly, nitryl chloride is formed by the action of the penta-chloride on nitric acid $NO_2OH + PCl_5 = NO_2Cl + HCl + POCl_3$.

Another preparation of phosphorus oxychloride is from phosphorus pentachloride and pentoxide. It takes place according to the equation $P_2O_5 + 3PCl_5 = 5POCl_3$, if the two substances are mixed in the proper proportions and heated in a sealed tube.

* The method of allowing substances to act on one another in sealed glass tubes is employed when it is desired to use a fairly high temperature above the boiling point of one of the reacting substances under atmospheric pressure. The necessity for a higher temperature occurs when the reaction does not proceed *quickly* enough at lower temperatures. Even in the case of substances sealed up in glass tubes which must be made of strong glass and carefully sealed off, the volatile substance, it is true, will partially vaporise ; the pressure in the interior of the tube, however, thereby rises, and with it also the boiling point, so that the greater part of the substance does not pass into vapour.

* The pressure hereby produced has, in general, only a slight influence on the chemical reaction ; the essential point is the possibility of raising the temperature without the substance evaporating.

The heat of formation of phosphorus oxychloride is 611 k_j.

369. Phosphorous Acid.—When phosphorus trichloride is de-composed with water, there is formed the compound PO_3H_3, which has acid properties and is called *phosphorous acid*.

The reaction which leads to the formation of phosphorous acid is represented by the equation $PCl_3 + 3H_2O = P(OH)_3 + 3HCl$. It takes place with great rise of temperature, and this can easily effect a further decomposition of the phosphorous acid. It is, therefore, expedient to use *concentrated hydrochloric acid* in place of pure water. The hydrogen chloride formed will then not be dissolved but will escape as a gas.

the heat of reaction will thereby be diminished by the amount of
heat of solution of hydrogen chloride. The resulting acid liquid
freed from the excess of hydrochloric acid by evaporation on the
water bath, and the pure phosphorous acid, melting at 74°, crystallises
from the liquid on cooling.

Since phosphorous acid contains one combining weight less oxygen
than phosphoric acid, it can, by taking up oxygen, pass into the latter;
it then acts as a reducing agent. On being heated, it acts in this way
on itself, whereby a portion is reduced to hydrogen phosphide:
$H(O)_4 = 3H_3PO_4 - PH_3$. We have here assumed the formation of
phosphoric acid; as a matter of fact, this simultaneously loses
water and passes into metaphosphoric acid. The corresponding change
in the equation can be easily made. The hydrogen phosphide which
formed takes fire at the temperature of decomposition, and burns
with a greenish flame.

Phosphorous acid also behaves as a reducing agent in aqueous
solution and withdraws oxygen and halogen from many substances.
Thus the silver and mercury salts, more especially, are reduced
to the metals, which are precipitated from the solution. This
action is used more especially for the detection of dissolved
mercury compounds.

In neutralising phosphorous acid with the aid of litmus or any
other indicator, no sharp transition is obtained. The liquid becomes
blue before the second equivalent of caustic soda or potash has been
added, so that, at most, only two combining weights of hydrogen of
the acid can be replaced by metals in aqueous solution, and even in
the solid state, no salts of phosphorous acid are known in which more
than two combining weights of hydrogen are replaced. Phosphorous
acid is, therefore, regarded as a dibasic acid, and normal *phosphoson* has
the formula PO_3H'.

This behaviour can be expressed by assuming that the two
replaceable hydrogens are joined to oxygen to form hydroxide,
whereas the third is united directly to phosphorus. This would

$$OP \begin{matrix} OH \\ OH \\ H \end{matrix}$$

give the formula OP·OH. According to this, phosphorous acid
would be a derivative of phosphoric acid, in which one hydroxyl
is replaced by hydrogen.

The circumstance, however, that phosphorous acid is formed
quite smoothly by the action of water on phosphorus trichloride,
speaks against this. The formation of the acid by water is a
typical reaction of the acid chlorides; these, on the other hand,
are derivatives of the acids formed by the replacement of hydroxyl
by chlorine. According to these reactions, phosphorus trichloride
ought to be the chloride of phosphorous acid, and this ought, there-
fore, to have the formula $P(OH)_3$.

* These contradictory views are not irreconcilable. It is not necessary that all the hydrogen which is present in hydroxyl should be replaceable by metals. According to what was said on p. 271, the gradual dissociation of a polybasic acid must take place with greater difficulty with each successive step. We have here a case where the last stage is so difficult to attain that, under normal conditions, no replacement of the third hydrogen by metals occurs, and the formula $P(OH)_3$ can be quite well reconciled with the dibasic nature of phosphorous acid. If it is desired to give expression to this, the formula can also be written $H_2PO_2(OH)$.

* The foregoing discussion furnishes an example of how attempts are made to express the so-called "constitution" of a compound by the way in which the formula is written. By this is meant that the formula is written in such a way as to give expression to the more important reactions of the substance in question, so that these can be easily read out of the formula.

* The means adopted for this consists in writing those elements which are often eliminated together in such a way that they appear side by side in the formula; they are sometimes still further separated from the other elements by means of a bracket or a dot.

* Such a separation can, for example, be very well carried out in the case of salts in respect of the two ions, and the formula of ammonium nitrate is, therefore, not written $N_2H_4O_3$, which represents the total composition, but in the form $NH_4 . NO_3$, to show that the salt when dissolved in water dissociates into the ions NH_4 and NO_3.

* In the case of the polybasic acids, which can form several ions, this separation causes some difficulty. In such cases it is carried out in such a way that all the hydrogen which could form hydrion if the dissociation were complete, is separated; thus, phosphoric acid is written H_3PO_4; in this way all the three hydrogens are made to appear as ions, although, in aqueous solution, the third hydrogen is dissociated only to a very slight extent. In the case of phosphorous acid, only two hydrogens are regarded as ions, although we are probably dealing only with a difference of degree, and not with an essential difference.

\# The demand for a universally valid formula can be still less made where we are dealing with oxy-acids which can, on the one hand, split off hydrion, and, on the other hand, when water is excluded, act as hydroxyl compounds. This is the case, for example, with sulphuric acid. This difficulty is overcome by employing different formulæ according to the reaction to which it is desired to give expression. Accordingly, sulphuric acid, as acid, is written H_2SO_4, or $H_2 . SO_4$; as hydroxyl compound, however, $SO_2(OH)_2$. In other words, the "constitution" of sulphuric acid cannot be represented by a single formula, and use is therefore made of more than one, according as they are required.

One might, perhaps, also unite the two formulæ by using the ... and stating the rule that the hydrogen attached to the oxygen hydroxyl is specially capable of being split off as hydrion. We would ... however, come back to the contradiction of phosphorous acid, ... from the fact that no splitting off of hydrogen can be detected in ... of the basic hydroxides.

The question must be asked, why it is that these relations give ... to such changing formulation, whereas many other relations could ... established with definiteness and free from contradiction. The ... is that it is here a question of representing very varied ..., the laws of which depend on many more variables than are ... in the chemical formula. The task consists, indeed, of ... a summary of all the transformations which one substance can ... with others; these transformations, also, so far as their result ..., are not quite definite, but depend to a large extent on ... conditions, such as temperature and pressure or concentration. ... these diversities cannot, of course, be represented by the simple ... of the relative arrangements of the elementary symbols, even ... the assistance of space, and a "constitutional formula" must ... always remain one-sided and be limited to the representation ... relations which have a special importance from their frequent ...

By the very careful oxidation of phosphorus in a slow current of ... a white substance is obtained, which differs from the phosphorus ... by its low melting point ($22 \cdot 5$), and its volatility (boiling ... 173). Analysis shows it to contain three combining weights of ... to two of phosphorus; determinations of the vapour density, ..., give the molar weight as 220, and lead, therefore, to the ... P_4O_6. It is the *anhydride of phosphorous acid*, for

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$
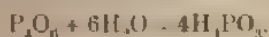
170 **Hypophosphorous Acid.**—The salt of this acid is formed ... with hydrogen phosphide by the action of caustic soda or caustic ... on phosphorus (p. 359). The reaction takes place according ... the equation

$$4P + 3NaOH + 3H_2O = 3NaPO_2H_2 + PH_3.$$
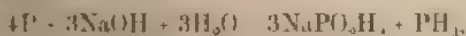
... the salt produced is found in the solution. For the purpose of ... the acid, barium hydroxide is used; this acts in a quite ... way, and gives rise to a solution of barium *hypophosphite*. The ... is obtained pure by evaporation and recrystallisation, and is then ... with the requisite amount of sulphuric acid. From the ... solution, the free acid is obtained by careful evaporation as a ... mass, which melts at 17, and is very soluble in water.

Hypophosphorous acid has the composition H_3PO_2; of the three

combining weights of hydrogen, however, only one can be replaced by metals, so that the acid is monobasic. Hypophosphorous has therefore the formula PO_2H_2'.

In its other reactions, hypophosphorous acid is very similar to phosphorous acid. Like it, it is a reducing agent which precipitates noble metals from their solutions; also, on being heated, it evolves hydrogen phosphide, which immediately ignites.

The salts are almost all soluble in water, so that none of them can be used for the identification of the acid.

An oxygen compound of phosphorus, which would correspond to the *anhydride* of this acid and would have the formula P_2O, is not known.

371. Hypophosphoric Acid.—In the acid liquid which phosphorus yields on being left exposed to moist air, there is contained, besides phosphoric and phosphorous acids, a compound which is intermediate between these two; this is called *hypophosphoric acid*, and has the composition $H_4P_2O_6$. As can be seen from the formula, it is a tetrabasic acid; hypophosphamon has the formula P_2O_6''''.

The acid is obtained from the above mixture by partly neutralising it with caustic soda and allowing to stand; the acid sodium salt $Na_2H_2P_2O_6$ then slowly separates out, and this is converted into the sparingly soluble lead salt which can be decomposed by means of sulphuric acid or sulphuretted hydrogen.

Hypophosphoric acid behaves, in general, similarly to phosphorous acid, but its reducing properties are less pronounced. On being heated the free acid, like all the lower acids of phosphorus, passes into phosphoric acid, with simultaneous evolution of hydrogen phosphide, which partly burns and partly decomposes into hydrogen and red phosphorus.

372. Lower Oxides of Phosphorus.—Various investigators have repeatedly prepared substances similar in appearance to red phosphorus, and have claimed them to be lower oxides of phosphorus. Since they have all been obtained as insoluble and non-volatile residues, their purification and characterisation are difficult, so that it is still doubtful whether one is dealing with pure substances.

373. Sulphur Compounds of Phosphorus.—When white phosphorus and sulphur are brought together, yellowish liquids are obtained which fume in the air and are readily inflammable. These were for a long time regarded as compounds of phosphorus with sulphur, but it has been found that they are only *solutions* of the one element in the other. Since the melting point of every solid substance is lowered by the solution of another substance in it, this must also be the case with phosphorus when sulphur is dissolved in it. The impression that chemical combination had taken place here was caused only by the fact, that the melting point of the phosphorus, which, for the pure substance, is 44°, is hereby depressed to below room temperature, so that the solutions comparatively rich in sulphur remain liquid.

Compounds of the two elements, however, corresponding to the [oxy]gen compounds of phosphorus, are obtained by allowing them to [act] on one another at a moderately high temperature. With white [phos]phorus so much heat is thereby developed that dangerous explo[sions] can occur; if red phosphorus, which contains much less energy, [is em]ployed, the heat development is correspondingly less, and the [proc]ess can be easily kept under control.

The two substances are mixed in the proportions corresponding [to] the formulæ P_2S_3 and P_2S_5, the mixture placed in a glass flask, [and] the latter heated at one spot. Combination then proceeds [slow]ly, but without explosion, through the whole mass. The re[sult]ing compound is, at first, liquid, but soon solidifies to a yellow [or] crystalline mass. The two compounds P_2S_3 and P_2S_5 can [scar]cely be distinguished by their appearance. The yellow-grey [colo]ur is due to contamination with red phosphorus; the pure com[poun]ds are yellow, crystalline masses which look like sulphur, but [pa]ler in colour.

The compounds do not take fire spontaneously in the air; on being [gen]tly heated, they burn to sulphur dioxide and phosphorus pentoxide. [They] smell of sulphuretted hydrogen, because they are converted by [the] water vapour in the air into this gas and phosphoric or phosphorous [acid:] $P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S$. They act similarly on com[poun]ds containing hydroxyl, and convert these into the corresponding [sulph]ur compounds.

Besides these compounds, there are still two other sulphides of [phos]phorus, the composition of which is represented by the formulæ [P_4S_3?] and P_4S_7. They can be obtained pure by melting the two [eleme]nts together in the proper proportions and distilling under [redu]ced pressure.

A coarse mixture of various sulphides of phosphorus has recently [bee]n used for the manufacture of matches, as these substances do not [hav]e the poisonous action of white phosphorus (p. 359).

In view of the analogous composition of phosphorus pentasulphide [and] the corresponding oxide, it may be asked if acids cannot be [obtai]ned from the sulphide, as can be done in the case of the oxide. It [is] very probable that there exists a whole series of acids corresponding [to] the oxygen acids of phosphorus, and containing sulphur in place of [oxy]gen. They are, however, very slightly stable, since they are con[vert]ed by water into the corresponding oxygen compounds, with [separa]tion of sulphuretted hydrogen. We shall, therefore, not enter [into] a discussion of these compounds, especially as similar compounds, [which are] more stable and better characterised, are met with in the case of [arse]nic, and will be then discussed.

Great stability, however, is possessed by *phosphorus sulphochloride*, [a] sulphur compound corresponding to phosphorus oxychloride. This [has the] composition $PSCl_3$, and can be obtained by heating phosphorus

fulfilled. In the case of the follo...   ...ng to the sam.
done :   ...r their form:

H—H ; Cl—Cl ;   Br—Br .   ... H₂O
H—F ; I -Cl ;   O = O ; S   ... H₂O.
H—S—H ; H—Se—H ; I.
Cl -O—O—H ;   Cl—O—O   means exist
                                       ...st import... ...

Cl—S—S—Cl ;   Cl—S—Cl
   ∕S ＼
O—O—O ;   H—S—O
H—S—O—O—O—O— H
H—O—O—S—O—O— H
of sulphur, selenium, and ...

$$N \equiv N ; \quad \begin{matrix} P = P \\ | \quad | \\ P = P \end{matrix} \quad \begin{matrix} As — A \\ | \\ As \end{matrix}$$
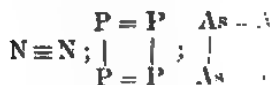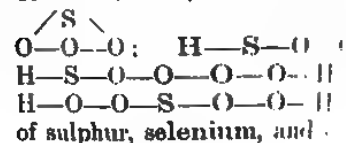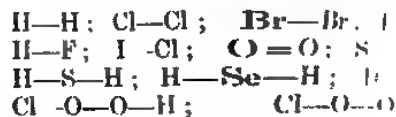
On the other han...
pounds
              SCl₄, Se...
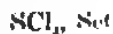
and many others.
    Various attempts ...
chiefly by assuming
Thus, the above sulp...
referred to a tetra...
compounds, at least ...

CHAPTER XVI

CARBON

General.—Carbon is one of the most important elements in respect both of the variety and wide distribution of its compounds and of the importance which these have in nature as well as in the arts. Although oxygen, hydrogen, and nitrogen are never failing constituents of living or organised structures, still carbon is frequently called the *organic element par excellence*, because it is on the combining relations exhibited by this element that the diversity of the substances of the organic kingdom most essentially depends.

But the pre-eminent importance of carbon is due not only to its being a constituent of the substances of which the structures of living things are built up, but much more to its being the expression of the supply of energy which is expended in vital action. For a similar reason, carbon is of importance in the arts, for by far the greatest part of the chemical energy which is set in motion for the accomplishment of the most diverse ends is derived from the chemical transformations of carbon.

Elementary carbon occurs in three different forms, which exhibit relationships to one another similar to those found in the case of sulphur or phosphorus. It exists in two crystalline forms and also in an amorphous state. The different varieties of amorphous carbon are usually, but probably incorrectly, classed together as one kind. Indeed, there are important reasons for thinking that there are several kinds of amorphous carbon, each possessing different properties, but none of which are known in the pure state.

That which is called *charcoal* is amorphous carbon in a more or less pure state. On heating organic substances, *e.g.* substances derived from organisms, especially plants, and containing carbon, a residue of this element is generally obtained, whereas the other elements present especially oxygen and hydrogen, escape in the form of water and lower carbon compounds of these elements. Moreover, the residue contains any non-volatile substances which may be present, as well as residual quantities of hydrogen and oxygen, which are larger amount the lower the temperature of carbonisation.

In the charcoal produced, the structure of the material can in some cases, *e.g.* when obtained from wood, be recognised; wood charcoal exhibits every cell of the wood well preserved. This is due to the fact that at the temperatures which are reached under these conditions carbon is an *infusible substance*. If the original material has also the same property of infusibility, as is the case with the substance forming the cell walls of wood, the form is well retained on carbonisation. In other cases, where the original material liquefies either before or during carbonisation, *e.g.* in the case of sugar, the charcoal which is obtained has the appearance of a mass which has been fused; this, however, is due only to the fact that sugar, not carbon, is fusible.

Sugar charcoal is much purer than wood charcoal, because in it the presence can easily be avoided of non-volatile impurities which are present in the case of wood charcoal, and which, on complete combustion, remain behind as a grey powder, the *ash*.

Soot is a still purer form of carbon. This is obtained by the combustion, in a small supply of air, of volatile compounds of carbon and hydrogen, of which there are a large number. The hydrogen then combines with the oxygen present, and the carbon is deposited and can be collected in the form of a very fine and light powder. Small quantities of hydrogen compounds which it still contains can usually be got rid of by igniting it with exclusion of air.

The properties of this form of carbon are the well known black colour, a small density, easy combustibility, small conductivity for heat and electricity, and a low degree of hardness.

All these properties, however, cannot be stated in definite numbers, but are found to vary to some extent, and that, indeed, in the following way. The higher the temperature to which the amorphous carbon was exposed, and the longer that temperature was allowed to act on the carbon, the greater are the density, hardness, conductivity for heat and especially for electricity, and the less is its combustibility. At the same time, the deep black colour passes into a grey one with a somewhat metallic lustre.

It has not yet been settled whether the cause of these changes is that the small particles of which the charcoal consists unite together or "sinter," at the high temperature to larger particles, or that there are *different forms* of amorphous carbon which occur mixed together in charcoal, the harder, more dense, and better conducting of which form are increasingly produced at higher temperatures. The melting point of charcoal is certainly as high as 3000 or 3500, the temperature of the electric arc, but it is quite possible that the general property of amorphous substances, of having no definite melting point, is present also in this case, and that, therefore, even at much lower temperatures, an incipient softening may occur which would lead to the formation of larger grains by the caking together of the smaller. In this way, the above mentioned changes can be partially explained. It appears

ever, especially in view of the increase of the hardness and con
ivity, to be more appropriate to assume the existence of several
as of amorphous carbon, which differ from one another in the
y described, and which in varying proportions make up ordinary
coal

Carbon retains the solid state with especial obstinacy. Only at
temperature of the electric arc, about 3500, does softening and
atu-ation occur. Further, there is scarcely a solvent which dis-
es carbon to any great extent. The only better-known one is
and iron, in which carbon dissolves to the extent of a few per cent
comparatively high temperatures, and from which it separates out
on the metal solidifies. Under these conditions, however, carbon
es not appear in amorphous form, but in the crystalline form of
plate which will be described later.

When heated in the air, carbon unites with oxygen, and is con-
ted into *carbon dioxide.*

The *coal charcoal* occurring in nature, such as *anthracite, coal,*
at *brown coal,* consists, it is true, chiefly of carbon, but it also
ains hydrogen and oxygen along with small quantities of nitrogen,
phor, and very varying amounts of ash, *i.e.* mineral admixtures of
il kinds. The different sorts have all been formed in a similar way
as of charcoal, viz. from the remains of previous vegetation by the
gradual loss of the other elements and the formation of a residue of
arbon. This process has, however, taken place at a low temperature
and required very long periods of time. This process of carbonisation
as progressed furthest in the case of anthracite, which contains only
little small quantities of hydrogen, not so far in the case of ordinary
coal, and least of all in the case of brown coal. The latter substances
cannot be regarded as carbon in the strict sense; on the contrary,
they consist of derivatives, of complex composition and certainly very
rich in carbon, of the substances of which the original plant-structures
were built up, or of mixtures of such substances with amorphous carbon.

On heating ordinary coal with exclusion of air, the hydrogen is
evolved in the form of carbon compounds This process is carried
out on a large scale for two purposes. On the one hand, coal rich
in hydrogen is subjected to heating or "dry distillation," and the
gases containing carbon which are produced are collected in order to
be used, after purification, for illuminating or heating purposes. This
manufacture of *coal gas* plays a very important part, since gaseous fuel
possesses important advantages over the solid or liquid. We shall
enter into this more fully later.

On the other hand, coal which is poor in hydrogen is also subjected
to dry distillation in order to obtain in the residues carbon which is
almost free from hydrogen, and which in many cases, especially for
metallurgical purposes, is to be preferred to coal containing hydrogen.
These coal residues are called *coke,* and are made on a very large scale.

A point which is of essential importance here is that the greater portion of the sulphur present is removed in the carbonisation, so that in this respect also a purification is effected.

377. Adsorption by Charcoal. The porous and cellular character which amorphous charcoal frequently assumes, when produced from organic structures of a corresponding form, develops a property which is possessed, indeed, by all substances, but which, in this case, appears with especial distinctness. This is the power possessed by porous charcoal of absorbing dissolved and gaseous substances from mixtures, and so freeing these gas mixtures or solutions from certain components.

If, for example, wine, litmus solution, or similar coloured solutions are shaken with finely porous charcoal (the most suitable being *bone charcoal*, obtained by carbonising bones), and then filtered, the liquid passes through the filter either quite colourless, or, at least, considerably lighter in colour. Likewise, from turbid, impure, or evil-smelling water there is obtained, by filtration through charcoal, clear water which has lost its smell entirely or to a large extent. For such purposes of purification, charcoal is largely used both in the arts and in the laboratory.

The processes with which we are here dealing are called *adsorption*, and depend on the fact that at the surface of contact between a solid body and a solution, a different concentration of the dissolved substance is produced from that in the interior of the solution. In many cases, the concentration of the dissolved substance at such bounding surfaces is greater than in the rest of the solution, but the opposite can also occur.

The cause which produces this action is of the same kind as that which effects *wetting*. The bounding surfaces between different bodies are, generally, the seat of a peculiar kind of energy which is called *surface energy*. The phenomena of surface tension or the phenomena of capillarity represent only a small portion of the actions of surface energy; indeed, this comes into operation in all cases where different bodies come together, or where *surfaces of separation* are present.

If, now, certain substances have the property of becoming specially concentrated at a bounding surface, they will be removed from a solution in which they are present when such bounding surfaces are formed in the solution. This is the case with charcoal and the above-mentioned colouring matters. A definite equilibrium is established between the portion in the solution and that absorbed on the charcoal, the greater part going to the charcoal.

This action depends, in the first place, on the nature of the dissolved substance, but to some extent also on the nature of the solid body. Substances of complex composition generally possess, to a comparatively much greater extent, the property of becoming concentrated at the bounding surfaces, whereas more simple substances

main chiefly in the solution. Since, now, most of the colouring matters which appear as unwelcome companion products in the preparation of organic substances have a very complex nature, they can be frequently removed from the solutions by this means. The method is employed with very good results, for example, in the sugar refineries, in order to so far decolorise the dark brown beet juice that white sugar can be obtained from it.

The same holds also for the malodorous products of decomposition of organic bodies, animal excremental matter, etc., which, on account of their complex nature, are also, as a rule, abundantly absorbed by charcoal.

Finally, what has just been said holds also for gas mixtures. Gases also condense to a more or less considerable extent on the surfaces of solid bodies, and again, the more complex and denser gases do so generally much more than the simple and light ones. The former can, therefore, also be removed more or less completely from mixtures with the other gases.

Since the action takes place at the bounding surface between the solid body and the liquid or the gas, it is proportional to the surface. The amount which 1 sq. cm. of surface can retain in this way is very small; in one special case (that of ammonia on glass) it has been found equal to $\frac{1}{2,500000}$th gm. pro sq. cm. Even if in the case of other substances the number can become ten or a hundred times as great, still the amounts with which we are here dealing are always exceedingly small. To obtain measurable amounts, therefore, very large surfaces must be employed ; for the absorption of one gram of ammonia a square surface of 50 metre side is necessary. Such large surfaces are found only in the case of very fine powders, or of very finely cellular structures.

This quality is possessed by bone charcoal, because bones contain, besides the organic matter of a gluey nature, large amounts of calcium phosphate. On carbonisation, the cellular structure is very completely preserved by means of this embedded matter, and if the calcium phosphate is removed by solution in hydrochloric acid, a fairly pure charcoal is obtained which for a given amount of substance possesses an exceedingly large surface, and therefore exhibits the phenomena of absorption with especial distinctness.

" If organic substances, e.g. sugar, which do not themselves yield on carbonisation a charcoal with largely developed surface, be mixed with calcium phosphate or similar infusible and readily removable salts, a strongly absorbing charcoal is obtained by the carbonisation of such mixtures, after removal of the admixed substance. In this case a large development of surface has been artificially caused, and with also, the corresponding action obtained.

Another action which is connected with the one just described, the *catalytic acceleration*, especially of gas reactions, which is exerted

by substances with largely developed surface. Thus, the oxidation of many substances by free oxygen is greatly accelerated when charcoal is present. Likewise, gases which under given conditions act only slowly on one another, can be made to act more quickly with the help of charcoal. In these cases, however, the actions of charcoal are greatly surpassed by the analogous actions of spongy platinum.

378. **Graphite.**—Graphite is a *crystalline* form of carbon. It occurs in nature as black-grey masses with a feebly metallic lustre, and crystallises in forms belonging to the hexagonal system; it is found in various localities, especially in Bohemia, Cumberland, and Siberia. Its density is 2·25. It is distinguished from amorphous carbon by its greater density, its good conductivity for electricity, and the great difficulty with which it burns. It is possible to effect its combustion only by heating it to a bright red heat in a current of oxygen. From the denser and better conducting forms of amorphous carbon, it is distinguished by its very low degree of hardness. This circumstance makes it probable that amorphous carbon which has been strongly heated and has thereby become a conductor, does not owe this property to the formation of a certain amount of graphite, for such carbon becomes at the same time very hard and does not give a black streak as graphite does.

Graphite can also be obtained *artificially* by allowing carbon to crystallise out from *fused metals*. It has already been mentioned that this is best known in the case of *iron*, but there are other metals which dissolve small quantities of charcoal when heated, and from which the latter separates at lower temperatures in a crystalline form as graphite. In the arts, graphite is prepared by heating charcoal mixed with lime to a high temperature for a long time in the electric furnace. The lime catalytically accelerates the transformation into graphite, probably by giving rise to an intermediate compound (calcium carbide, p. 411).

Graphite, also, must be divided into different groups which exhibit a somewhat different behaviour. It has, however, not yet been settled whether these differences may not perhaps be due only to mechanical differences, the one form consisting of innumerable laminæ laid closely together, while the other forms more coherent masses. We shall here, therefore, refrain from entering on a discussion of these differences.

Graphite agrees with amorphous carbon in its resistance to fusion and volatilisation at comparatively high temperatures. It is used, therefore, for making *crucibles* which have to withstand especially high temperatures, and for this purpose it is mixed with some clay to act as binding material and then moulded. The slight combustibility of graphite allows of such crucibles being heated without special precautions even in the air.

Some further applications of graphite are due to its property of being split into thin scales. *Lead pencils* are made from graphite, the

... being finely powdered, and, by admixture with clay or other ... material, formed into the well known thin rods, to which ... is imparted by slight firing. According to the amount of ... added, the pencil has varying hardness.

Further graphite is used as a *lubricant*, and this also depends on ... disintegration into smooth scales. These fill up any uneven ... in the rubbing surfaces and quickly form a smooth coating, ... effects an easy gliding. Where it can be applied, graphite ... the advantage over grease of being insensitive to differences of ... ature.

Diamond.—A second crystalline form of carbon is the ... In contradistinction to the two other forms, diamond is ... parent and colourless, but possesses the power of strong refrac... and dispersion, so that, when cut into regular forms, it exhibits a ... lustre and play of colours, to which its use as a gem is ... That it consists of pure carbon is seen from the fact that it ... on combustion carbon dioxide, and this also in exactly the ... proportions as any other form of pure carbon

Diamond crystallises in the regular system chiefly in octahedra, ... often exhibit somewhat rounded edges. Its density is 3·5 ... property which is most important for its applications is its great ... In this respect it is superior to all other naturally occurring ... and also to most of those that can be artificially prepared. ... used for cutting glass, for drills for working in hard rock, for ... used for turning very hard steel and emery discs, etc. A ... rotating disc of tin plate or of copper into which diamond ... have been pressed, cuts glass and other hard substances with ...

According as it is desired to use the diamond for *writing* on or ... glass, differently formed pieces must be used. For writing, ... any point may be used which when properly held will scrape ... from the surface of the glass, and according to the sharp... of the point and the pressure employed, the finest lines can be ... For cutting glass, the diamond must have a chisel shaped ... which will cleave the glass; such a diamond cuts, therefore, only ... definite position, and must be held accordingly

Diamonds occur rather rarely in nature, so that their price is high. ... artificial preparation has recently been successful, but has as yet ... only macroscopically small crystals. Diamonds are obtained ... iron which contains carbon and allowing this to fall in small ... into water so that it is suddenly cooled. If the iron is ... dissolved a small quantity of a crystalline dust is left whose ... hardness, resistance to the action of chemical agents, and ... on heating, show it to be composed of diamond. In ... 100 such artificial diamonds are shown as seen under the ... scope.

Although the pure diamond is colourless, diamonds of all possible colours, especially yellow, and from brown to black, occur in nature. The latter, which have no value as gems, are used for technical purposes. The colours are due to impurities, especially organic substances.

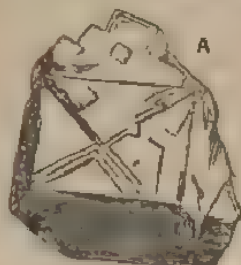As regards the mutual stability relations of these different forms of carbon, we possess as yet no exact knowledge, for the transitions take place with such excessive slowness that it is hardly possible to follow them experimentally. The following has been established with some degree of certainty.

Amorphous carbon must be regarded as the least stable; it contains the greatest amount of energy. Graphite must, very probably, be regarded as the most stable at comparatively high temperatures. The reason for this is, especially, that at very high temperatures diamond passes into graphite. Accordingly, diamond would, with respect to stability, stand in the middle.

However, as is known, the relative stability of different forms of the same substance depends very much on the temperature, and it is, therefore, not admissible to directly draw conclusions as to the relations at ordinary temperatures from those existing at 3000°.

380. Compounds with Oxygen.—Carbon forms two oxides, one combining weight of carbon being able to unite with one or with two combining weights of oxygen. The second of these compounds is by far the more important.

Carbon dioxide, CO_2, is a gas with the normal weight 44; it is colourless, has a feeble but distinct taste and smell, and dissolves fairly readily in water. At room temperature, water absorbs about an equal volume of the gas. With changes of pressure and temperature, carbon dioxide shows appreciable deviations from the simple gas laws; by increase of pressure it can be readily liquefied. In the following table the vapour pressures of carbon dioxide are given; these are equal to the pressures which must just be exceeded in order that the gas may pass into a liquid.

Temperature.	Pressure.	Temperature.	Pressure.
80	1·00 atm.	- 10	26·76 atm.
70	2·08 „	0	35·40 „
60	3·39 „	10	46·05 „
50	6·80 „	20	58·84 „
40	10·25 „	30	73·44 „
30	15·15 „	31	75·48 „
20	19·93 „		

As can be seen from this table, the pressure of liquefaction at 0 ... equal to 35 atm.; at −80 the pressure of 1 atm. is sufficient, in order to liquefy the gas. The critical temperature is 31 , this is the limit up to which the conversion of the gas to a liquid can be effected by pressure.

381. The Critical Phenomena.—Since it was in the case of carbon dioxide that the critical phenomena were first discovered in their mutual connection, it will be appropriate to discuss them more fully at this point. This will be best done with the help of a diagram representing the relation of *pressure* and *volume*.

In Fig. 101 the volumes are measured to the right and the pressures upwards. For every temperature there will then be a line which will represent the corresponding values of pressure and volume. If, therefore, any definite temperature is taken, there will correspond to each pressure a definite volume, and *vice versa* ; all the corresponding values of these will be represented by a connecting line, which is called an *isotherm*, because it is a line of constant temperature.

For liquids, the isotherms have the following form. If the pressure weighing on a liquid be changed, the volume changes in the opposite sense, but only to a very small amount, because the compressibility of liquids is very small. If, therefore, in the above mentioned diagram, we measure the volumes to the right and the pressures upwards, we obtain an almost perpendicular line, since almost identical volumes correspond to very different pressures, and the former, therefore, lie almost exactly under one another. On account of the slight increase of volume with diminishing pressure, the isotherm for liquids inclines slightly to the right, if we follow it from above downwards, that is, in the direction of smaller pressures. In Fig. 101, the line marked 13·1 shows on the left such a liquid isotherm.

At a definite minimal pressure, vapour begins to form from the liquid. If we now attempt to diminish further the pressure by increasing the volume, we do not succeed in this, but more vapour forms, and the pressure remains, so long as both liquid and vapour are present, constant. A line representing constant pressure being, as we saw, is a *horizontal line* in our diagram. For the range in which liquid and vapour, the isotherm is therefore a horizontal line, as the portion of the line 13·1 in Fig. 101. ... On increasing the volume, all the liquid finally evaporates ... vapour is present. So soon as this occurs, the pressure falls when the volume increases, to a much less extent ... The vapour formed follows approximately the ... const., and the isotherm is represented ... in Fig. 18, p. 77, is a hyperbola. This ... 31° in Fig. 101.

If now we apply the same consideration ... higher temperature, we may, to begin with ...

word for word. The difference which exists consists in the fact
the volumes of the liquid, on account of the higher temperature
rather greater than previously, under the same pressures; the lo.

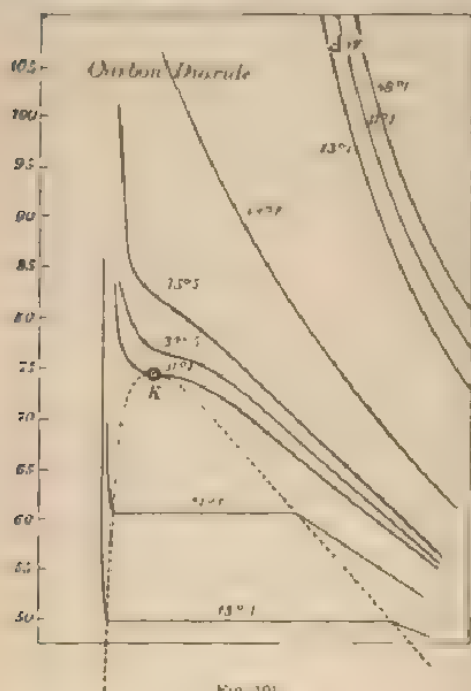isotherm, therefore,
to the right of the pre
vious one. Further
vapour, on account of
higher temperature, ap
pears at a greater press
the horizontal portion
the isotherm, there
starts higher up, t.
previously. Finally
liquid entirely evapor
at a smaller volume, b
even if on account of
higher temperature th
vapour should have, at
given pressure a sma
density, still the in rea
of the vapour pressur
by which the volume
diminished, amounts
much more, and the to
result is a considerab
diminution of the volum
of the vapour. T
form for such an isotherm
at a higher temperatur
is represented in Fig. 1

Fig. 101

by the curve marked with 21·1, in which the above mentione
differences from the lower isotherm for 13·1 can be seen.

The higher, now, the temperature is taken, the nearer do the tw
ends of the horizontal straight lines come together, i.e. the less do the
volumes or the densities of the liquid and of the vapour differ from
one another. On the isotherm 31·1 the two finally come together in
the point K.

The meaning of this is that in the point K, *the densities of liqui
and vapour have become equal*, and since, apart from this, the compos
tion and chemical nature are the same, the two states become com
pletely *identical*. At this point, the *critical point*, therefore, the
distinction between liquid and vapour disappears.

At still higher temperatures the isotherms, of which there are still
some in the diagram, have no horizontal middle portion but are con
tinuous. *Here, accordingly, the phenomena of liquefaction and evaporation
are no longer possible, and all changes of state take place continuously.* At

first the proximity of the critical point makes itself still evident in the flexures of the isotherms, as is clearly shown in the isotherms 32·5 and 35 5 ; at 48·1 , however, these have also disappeared, and the isotherms no longer differ essentially from those of a gas.   The corresponding isotherms for air are inserted to the right at the top of the diagram ; these show that carbon dioxide, under the high pressures employed, deviates from the gas laws in such a way that the volumes are considerably smaller than in the case of a perfect gas.

The region enclosed by the curved, dotted line, in which the horizontals representing the states liquid plus vapour lie, can be called the region of *heterogeneous states*, since in it *two* phases are present. Everywhere else, there is only *one* phase present · at the left edge, liquid ; at the right, vapour.   The diagram shows that *above the critical point these two latter regions are continuously connected with one another.* In other words, it must be possible to convert a liquid into a vapour or a vapour into a liquid without the one ever being observed to separate from the other, or without liquid ever visibly passing into vapour, or *vice versa.*

To perform this, carbon dioxide is, we shall suppose, first compressed at a low temperature, so that it is completely converted into a *liquid.* One thus commences with a point which lies to the left of the region of heterogeneous states.   If, now, the pressure is always maintained high enough so as to remain in this region, and the temperature be raised above 31·1 , we always remain to the left of the central field but reach a point higher than the point K.   If the pressure is now diminished, while the temperature is maintained above the critical value, we pass to the right along one of the isotherms.   On this isotherm the pressure can be diminished to any desired extent, and the temperature also can be allowed to fall ; so long as one avoids coming into the *heterogeneous region*, the carbon dioxide is undoubtedly in the *gaseous* state, a fact of which one can convince oneself by reducing the pressure to that of the atmosphere and opening the vessel.

Similarly, just as along a path above the point K, a *liquid* can be converted continuously into a *vapour* or a *gas* without vapour ever making its appearance along with it, so it is possible to convert a gas continuously into a liquid *without a separation of liquid ever becoming visible.*   For that purpose, it is only necessary to raise the temperature above the critical value, and the gas can then be compressed without its liquefying.   Above the pressure corresponding to the point K, or the critical pressure, the temperature can be lowered below 31·1 .   If the pressure be now diminished, it is found that the substance exists in the liquid state.

The critical point K is characterised by three magnitud *critical temperature*, or the temperature of the isotherm in whi and vapour become identical ; the *critical pressure* correspon this ; and the *critical volume* or the *critical density.* The tw

are the values of the pressure and volume, or density, at the point
They are obtained from the diagram by reading off the correspon...
distances on the axes of pressure and volume.   Thus, the critical pr...
sure of carbon dioxide is found to be about 75 atm.   The crit...
volume has to be referred to some definite quantity of substance   f...
one mole, or 44 gm. carbon dioxide, it amounts to 112 cc.

Three such critical constants be ong to every pure substan...
Whereas the critical temperatures are to be found ranging from t...
lowest to the highest temperatures, the critical pressures move with...
fairly narrow limits, between 20 and 100 atmospheres, which th...
exceed only in quite exceptional cases.   The critical volumes of ...
mole are also not very different , like the other critical constants, th...
increase with the molar weight of the respective substances, and ...
from 10 to some hundred cubic centimetres.

382. Liquid Carbon Dioxide.   On account of the modera...
pressure by which carbon dioxide can be liquefied, even at the or... a...
temperature, this substance is now placed on the market in la...
quantities in the liquid form.   For this purpose, the gas is p...
into iron cylinders (Fig. 37, p. 104), which are kept cool, an...
thereby converted into the liquid state.   The starting material, ca...
dioxide gas, occurs abundantly in various localities.   Especial...
districts where volcanic activity, previous or existing, can be re ...
copious streams of carbon dioxide are frequently found escaping fr...
fissures in the earth, and this gas is suitable for being directly l quefi...
In Germany, such sources of carbon dioxide exist, especially in th...
Eifel district.

If liquid carbon dioxide be allowed to stream out into the a.r, pa...
of it immediately evaporates.   So much heat is thereby withdraw...
from the remainder that its temperature sinks below the point ...
solidification of carbon dioxide, and the latter solidifies in the for...
a white snow.   By allowing the liquid to stream into a bag of clos...
woven cloth, the "carbonic acid snow" can be filtered off, the so...
remaining in the bag while the gaseous portion escapes through ...
fabric.

The solid dioxide is used chiefly for producing low temperatur...
For this purpose it is mixed with ether, which still remains liquid at t...
temperature produced, and a paste is thus obtained whose temperatu...
is - 80 .   In a space pumped as vacuous as possible, the temperature ...
this freezing mixture sinks, in consequence of the accelerated evapor...
tion, to   100 .

383. **Solution in Water.**—In water, carbon dioxide dissolves ...
accordance with the law of Henry (p. 274).   The aqueous solution ...
an acidulous taste and causes a prickling sensation   The refreshi...
taste of spring water is produced essentially by the presence of car...
dioxide, which is present in abundance in most natural waters   ...
passes into these from the soil, where it is being constantly develo...

at the slow combustion of the organic substances by the oxygen of the air. Since the saturation with this gas has taken place at a low temperature, such waters are generally supersaturated, and when they become warmer by standing in the air, the gas slowly forms bubbles on the walls of the vessels. This formation of bubbles in water containing carbon dioxide is regarded as a sign of a palatable drinking water. It of course gives no security against the presence of other substances of a harmful nature.

Water in which carbon dioxide is dissolved in somewhat larger amounts frequently occurs in nature, and is used, as *aerated* or *mineral waters*, for medicinal purposes or as a beverage. Large quantities of water artificially saturated with carbon dioxide under the pressure of from two to three atmospheres are prepared, and are used, with addition of various salts, for the same purposes.

Liquids containing carbon dioxide are also produced in the fermentation of solutions containing sugar. In this process the sugar decomposes into *alcohol* and *carbon dioxide*, and in certain liquids of this kind, *e.g.* beer and sparkling wine, the fermentation is conducted in such a way that the carbon dioxide does not escape, but remains dissolved, in larger or smaller amounts, in the liquid.

For the preparation of aerated liquids, the gas was formerly chiefly prepared from naturally occurring compounds, the carbonates, by means of acids. At the present time, liquid carbon dioxide is chiefly employed, being manufactured in large quantities and placed on the market at a very low price.

344. Carbonic Acid. —The solution of carbon dioxide reacts feebly acid to litmus, the colouring substance being rendered not *bright red* but only *wine red*. This, however, is essentially due to the small concentration obtained in aqueous solutions of the gas under ordinary pressure. If the amount dissolved is increased by using higher pressure, a solution is obtained which also gives the ordinary bright red colour with litmus.

In the aqueous solution, therefore, there is an *acid* present, and carbon dioxide is to be looked upon as the anhydride of this acid. The relations are the same as in the case of sulphurous acid; the formula of carbonic acid is H_2CO_3, and it decomposes with extreme readiness into water and the anhydride CO_2, carbon dioxide or carbonic acid anhydride.

Carbonic acid is a *dibasic* acid with very slightly developed acid properties. Like the dibasic acids in general, it forms two *carbon ions*, the monovalent HCO_3' and the *bivalent* CO_3''. Since even the process $H_2CO_3 \rightleftharpoons H + HCO_3'$ takes place only to a very slight extent, the second stage of dissociation, $HCO_3' \rightleftharpoons H + CO_3''$, is, for most purposes, comparatively small. In aqueous solution, therefore, the monovalent ion HCO_3' is formed by preference, and to this some of the characteristic properties of the carbonates are due.

The *salts of carbonic acid*, or the *carbonates*, are mostly very diffi u
soluble in water ; only those of the alkali metals form an exceptio
and are easily soluble. The latter react fairly strongly alkaline, since
from the tendency of the ion CO_3 to interact with water and pass into
HCO_3' ($CO_3'' + H_2O$ $HCO_3' + OH'$), a certain amount of hydroxy
is produced, whereby the alkaline reaction is effected. On adding
of acids, all carbonates evolve *carbon dioxide*. Carbonic acid is at
formed, but this can exist in aqueous solution only to a small exten
and mostly decomposes into the anhydride and water $H_2CO_3 = CO_2 +
H_2O$. Since carbonic acid is, as has just been mentioned, a very feeble
acid, this reaction is brought about also by other weak acids, and
the power of expelling carbon dioxide from carbonates can almost be
considered as a characteristic of the acids.

385. **The "Circulation" of Carbon.**—In nature, carbonic acid
and the carbonates occur in very large quantities. The air always
contains carbon dioxide, the amount of which varies somewhat. In
places where there is no special source of the gas present, the amount
is about $\frac{1}{2000}$th of the volume of the air. This amount is increased
by organic respiration and combustion processes of all kinds ; added to
this, there are also considerable amounts of carbon dioxide derived
from volcanic action.

All organisms make up for the waste necessary for their vital
activity by the consumption of *chemical* energy, which, for the greatest
part, is the *energy of the oxidation of carbon*. Whereas animals and
those plants which do not contain chlorophyll can carry out the oxida
tion only of already existing carbon compounds, and live from these,
the green plants can also carry out the opposite process; *they as
decompose carbon dioxide into carbon (or compounds of carbon) and fre
oxygen*. For this a considerable expenditure of energy is necessary
and this the green plants derive from the radiant energy of *sunligh*
They thereby store up not only the supply of energy which they
require for their own life, but they also yield the supply of energy
which is used by all the other organisms and which these take up in
the form of food   By the oxidation of this carbonaceous food, first of
all the herbivorous and then indirectly through the medium of these
the carnivorous animals obtain their vital energy.

By means of the oxidation in respiration, the carbon again return
to the air as carbon dioxide, and a "*circulation of carbon*" is produced
by which the mutual preservation of the vegetable and animal kingdom
appears to be lastingly assured. However, for this end, it is not the
conservation of the *carbon* that is the real problem here; the role of
carbon is only to effect the transport of the *energy* with which it is
associated, which is the essential thing. In fact, certain organisms
are known, e.g. the sulphur bacteria, which obtain their vital energy
not from the oxidation of carbon compounds but by quite different
chemical reactions. There are, therefore, organisms which do not

ire any carbon for this purpose, no organism, however, is con
able which would not require to have *free energy* at its disposal in
r to exhibit any kind of vital activity.

So far, now, as our knowledge extends, *no such cycle exists for
us.* Here it is a case of a current flowing in one direction, which
is cast from the sun on to the earth, where it is partly *used up* and
partly *stored up* by the plants. The supplies stored up by the plants
for the greatest part further used up by the other organisms, but a
smaller part is preserved as fossil combustible material and serves in
our times as the most important source of energy in the industrial life
of man. That the free energy which is derived from the sun and
earth in this way is finally used up, will by any process be again made
available, we have no sign; on the contrary, from the experience
which has been gained with the terrestrial processes, it is to be
assumed as probable that such a reverse process, corresponding to the
spontaneous flow of a stream uphill, is not possible (p. 135). It is,
therefore, of essential interest for the permanent maintenance of life
that as large a portion as possible of the radiant energy of the sun
should be brought into the storable form of chemical energy, and that,
therefore, as large a part as possible of the earth's surface be covered
with green plants. As is well known, great improvements in this
respect are still possible.

If one considers that, as already mentioned, the amounts of energy
used in the industries are also derived for the most part from the
chemical energy of carbon, namely, in so far as they are obtained by
the combustion of coal or other fossil fuel, we see that this element is,
in fact, along with oxygen, the most important carrier of chemical
energy, indeed, of any energy whatever. It would be incorrect to
designate carbon alone as the carrier. The quantities of energy in
question become free only by *combustion, i.e.* when the carbon com
bines with oxygen, and we must not assert that the energy was
contained solely in the one or other element. In other words, we are
dealing with the energy equation

$$C + O_2 = CO_2 + 406 \, kj,$$
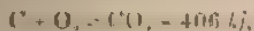
and for this, *each* member is of *equal* importance. Only, the carbon
usually appears to be the sole carrier of the energy because the oxygen
is generally accessible in the air and does not, therefore, require to be
specially prepared and bought. If the plants did not separate the
oxygen in the gaseous form but as a solid compound rich in oxygen,
the latter would be just as necessary for the conservation of life and
the heating of steam engines, as the solid carbon compounds; it, also,
could be consumed by animals, and would also be collected by man
and placed on the market.

386. The Combining Weight of Carbon has been determined

by combustion to carbon dioxide. The latter can be completely retained by a concentrated solution of caustic potash or soda and weighed. If, therefore, the carbon is weighed, and also the potash apparatus before and after the experiment, we can ascertain how much carbon dioxide has been formed by the combustion, and, by difference, how much oxygen has combined with the carbon. In this way, pure amorphous charcoal as well as graphite and diamond have been investigated; with all three, exactly the same ratio has been obtained, so that the different quantities of energy present in the different forms of carbon exert no influence on the combining weight. The uniform result of the determinations was that exactly 12.00 of carbon unite with two combining weights (32) of oxygen, so that we have to put $C = 12.00$.

387. **Detection of Carbonic Acid.** Although carbon dioxide on being dissolved in water yields only very feebly acid solutions, it readily forms salts with dissolved bases; it is, therefore, rapidly and completely absorbed by solutions of these. This behaviour is made use of for the detection and quantitative determination of carbon dioxide (e.g. in the air), and those bases more especially are employed which form insoluble carbonates. Most frequently there is used a solution of lime or calcium hydroxide, $Ca(OH)_2$, which forms with the dibasic carbonic acid the salt $CaCO_3$, or calcium carbonate. This is precipitated from the solution in the form of a white powder, and by means of it small quantities of carbonic acid can be detected.

The formation of this white precipitate is sufficient for the qualitative proof of the presence of carbonic acid. If a quantitative determination has to be made, a measured volume of the lime solution (lime water, the strength of which has been determined by titration with an acid (p. 190), is taken, and after the reaction has occurred the precipitate is allowed to settle, and the amount of lime remaining is determined in a measured portion of the clear liquid; the difference is a measure of the carbon dioxide absorbed.

388. **Derivatives of Carbonic Acid.**—Although carbonic acid itself is not known, there exist not only a large number of salts which contain carbanion, but also compounds formed by the replacement of its *hydroxyls*; more especially, the chlorides and amides of carbonic acid are known, some of which are of very great importance.

If carbonic acid be written as a hydroxyl compound, there are possible, on account of the presence of two hydroxyls, two chlorides and two amides, exactly as we found in the case of sulphuric acid (p. 305). Represented schematically, we have the following compounds :—

Carbonic Acid   Chlorides.   Amides.

$$CO \begin{cases} Cl \\ OH \end{cases} \qquad CO \begin{cases} NH_2 \\ OH \end{cases}$$

$$CO \begin{cases} OH \\ OH \end{cases}$$

$$CO \begin{cases} Cl \\ Cl \end{cases} \qquad CO \begin{cases} NH_2 \\ NH_2 \end{cases}$$

these substances are known, some, however, only in the form of compounds

The *carbon oxychloride*, $COCl_2$, or *carbonyl chloride* (the residue CO called carbonyl), is produced directly from carbon monoxide (p. 399) and chlorine, by mixing these two gases in equal proportions and exposing to sunlight. Here, as in many other cases, the action of chlorine is very markedly accelerated by the influence of light. To this is also due the name "phosgene gas" for carbonyl chloride. Since, however, the compound is also formed without the aid of light, we are not dealing here with the communication of a necessary energy, as in the case of the reduction of carbon dioxide in the green plants (p. 394) but merely with a case of *acceleration*; the light acts catalytically.

In defect of sunlight, *charcoal* can also be used as catalyser: combination likewise takes place, especially on passing the gaseous mixture over animal charcoal.

The reaction occurs in accordance with the equation $CO + Cl_2 = COCl_2$. That is to say, one volume of each of the two components unites to form one volume of the compound.

Carbon oxychloride is a colourless gas with a suffocating odour, and can be readily liquefied by means of a freezing mixture; it boils, under atmospheric pressure, at $+8°$.

Carbon oxychloride behaves chemically as a true acid chloride. It is decomposed by water, forming carbonic acid and hydrochloric acid, and by ammonia with formation of ammonium chloride and the amide of carbonic acid (*vide infra*).

The *acid chloride* of carbonic acid, or chlorocarbonic acid, ClCOOH, is usually called chloroformic acid, since the corresponding hydrogen compound, the monobasic acid HCOOH, is called formic acid. It is not known in the free state, but only as a constituent of more complex compounds; these belong to organic chemistry, and will, therefore, not be treated in detail here.

Amides of Carbonic Acid.—As has already been mentioned, the amide of carbonic acid is formed by the action of ammonia on

arc... ...ride, in accordance with the general reaction as rep... ...ted in the equation $COCl... + 4NH... = CO(NH_2)_2 + 2NH_4Cl$. The two substances can be separated by treatment with alcohol, in which the ... ...but the ammonium chloride, is soluble, and the carb... ...unde ... ... is obtained as white crystals which ... ...ble in water and have a cooling and somewhat bitter taste. T... ...tive ...ain character, and their aqueous solution does not con... ...the ...

The same substance is formed in the bodies of the mamm... ...especially the carnivora, as the final product of the metabolism of ... nitrogen which is contained in the food and consumed in vital action ...and ...is the organism dissolved in the watery excretion, the ut... from the urine of the carnivora, after being concentrated, it must ... ...from that of the omnivora, especially of man ... in this simple way, since its crystallisation ... ...in the presence of other substances. To the concentrated ...nitric acid is added, a difficulty soluble compound ... ...which crystallises out, and from which the substance ... ...obtained by converting the nitric acid into a salt by any base ... ...occurrence in urine, the compound is usually called urea

As ...salt of ...nic acid, urea has the property of passing, in ... ...with water, into the ammonium salt of carbonic a... $CON_2H_4 + 2H_2O = NH_4 CO_3$. At the ordinary temperature th... ...change is exceedingly slow; at 100°, however, appreciable amounts of ammonium carbonate are formed in an aqueous solution of urea, ... If acid is added, the transformation proceeds still more quickly, ...carbonic acid being evolved, and the corresponding ammonium salt remaining in solution. Strong bases have a similar action. In ...very often are present organic compounds possessing the power of ...acceleration, but of unknown composition, called ferments ... ... These have been formed by the schizomycetes which ...in the urine, and have the power of accelerating this absorp... ... ...water by urea, even in neutral solution. Sometimes such ...are present in the bladder of the living organism; the ammonium carbonate then formed has a corrosive action on the organism and can cause very severe illness.

On account of its occurrence in the animal organism, urea was ...with the ...compounds before its simple relation to ... had been discovered. Since the organic compounds were ...regarded as being produced under the influence of a special ... force, the actions of which, it was assumed, could not ... ...the organism, a great sensation was caused when ... ...Wöhler discovered a method of preparing urea artificially ... ...the transformation which the ammonium salt of cyanic ... ... in aqueous solution, and will be described somewhat ...

This first "synthesis" of an organic compound was followed later innumerable others, and although by no means all the compounds which occur in animals and plants have as yet been artificially prepared, still in the work which has been directed towards this end, no circumstance has been encountered which makes it improbable that, on more thorough investigation, it will be possible to artificially prepare the constituents of the organisms.

The other amide of carbonic acid has the formula $CO\begin{smallmatrix} NH_2 \\ OH \end{smallmatrix}$; it is, therefore, an acid, and is called *carbamic acid*.

Carbamic acid itself is not known. Its salts, the carbamates, are produced when ammonia and carbon dioxide come together in presence of bases. Thus, the calcium salt is obtained by adding ammonia to calcium hydroxide and passing carbon dioxide into the mixture. Since calcium carbamate, $Ca(OCONH_2)_2$, is soluble in water, while calcium carbonate is not, the formation of a soluble calcium salt in the above circumstances is a proof of the formation of the new salt.

The *ammonium salt* of carbamic acid is formed as a white crystalline mass on bringing ammonia and carbon dioxide together. This can be carried out directly with the two gases, or, more conveniently, the gases are passed into anhydrous alcohol, in which the ammonium carbamate soon separates out.

In accordance with the formula of the acid, the composition of the salt is given by the formula NH_4OCONH_2. If we write the summed formula we obtain $CO_2N_2H_6$, i.e. the sum of one mole carbon dioxide and two moles ammonia. This is the explanation why the salt can be formed directly by the union of the two gases.

By themselves, the carbamates, even in aqueous solution, are fairly stable, especially when the solution has an alkaline reaction. If, however, the liquid is acidified, an ammonium salt is formed and carbon dioxide is liberated. This reaction is represented by the equation $NH_2 \cdot H + CO_2 \cdot NH_3$, which shows that carbamic acid can pass into ammonia and carbon dioxide.

Carbon Monoxide.—When coal is burned in a restricted supply of air, a gas is formed which can burn in the air with a characteristic blue flame, forming carbon dioxide. This phenomenon is easily seen in a coal fire. When most of the hydrogen compounds present have been burned, and the coal has become quite incandescent, the coal lying at the foot of the grate which comes into contact with the incoming air, burns, it is true, to carbon dioxide, but this gas, on passing through the upper layer of glowing coal is, in accordance with the equation $CO_2 + C = 2CO$, reduced to the compound CO, which represents the above combustible gas. At the top of the glowing layer where abundance of air can again find access, the gas burns to dioxide with the above-mentioned blue flame.

This compound, therefore, can be obtained by passing carbon dioxide over strongly heated charcoal. Since in this process much energy is taken up, this must be communicated from without, i.e. the tube must be strongly heated. If the issuing gas is passed through a solution of caustic soda, the carbon dioxide which remains undecomposed is absorbed, and the residue is pure carbon monoxide. In order that this reaction may take place, the temperature must be above 700°. At lower temperatures, carbon monoxide passes into the dioxide with separation of carbon.

Carbon monoxide is a colourless gas with the molar weight 28; it must, therefore, have the formula CO. The density is equal to that of nitrogen, and most of the physical properties of the two equally dense gases also show close agreement. Thus, the critical magnitudes are :—

	Carbon monoxide	Nitrogen
Critical temperature . . .	$-140°$	$-146°$
Critical pressure . . .	36 atm.	35 atm.
Critical molecular volume . .		103 cc

The solubility of the two gases in water is also equally small.

Of the special properties of carbon monoxide, its poisonousness should be mentioned, which, in certain circumstances, makes it a very dangerous substance. This depends on the fact that the gas can combine to form a very stable compound with hæmoglobin, the colouring matter of the red blood corpuscles. Now, hæmoglobin has the function of taking up the oxygen inspired into the lungs and of conveying it through the blood canals to the parts of the body where, by its oxidising action on the different tissues and their constituents, it maintains vital activity. But if the hæmoglobin combines with carbon monoxide, it loses the power of taking up oxygen, and precisely the same effect to supervene as on suffocation.

Such cases of carbon monoxide poisoning easily occur when coal is burned in a stove which has an insufficient outlet, or if this outlet be closed. Every year such cases of poisoning occur through closing the stove register too soon. Carbon monoxide poisoning may also be occasioned by coal gas, which, on an average, contains 0·1 of its volume of carbon monoxide. Certain kinds of gas which are obtained by the action of steam on heated charcoal (water gas) contain much more carbon monoxide, and their use in daily life is, therefore, not without objection.

* The presence of carbon monoxide can be detected by the fact that it is so readily absorbed by hæmoglobin. If the gas to be investigated is passed into a solution of the colouring matter of the blood, the presence of carbon monoxide is shown by the appearance of two characteristic bands in the absorption spectrum of the colouring matter. These, it is true, appear similar to those produced by oxygen, but they can be distinguished from the latter by the fact that a

addition of reducing agents (e.g. sodium sulphide) they do not disappear, whereas the oxygen bands do.

With oxygen, carbon monoxide burns to dioxide in accordance with the equation $2CO + O_2 = 2CO_2$. Two volumes, therefore, of the monoxide unite with one volume of oxygen to yield two volumes of carbon dioxide, and in this respect the relations correspond exactly to those of detonating gas obtained from hydrogen and oxygen. With oxygen or air, carbon monoxide also yields a "detonating gas" or explosive mixture, which, however, burns much less violently than the former.

This is not in any way due to a smaller development of heat, the heat of combustion being in both cases almost exactly the same, for it amounts to 284 kj for one mole of carbon monoxide, and 286 kj for one mole hydrogen. The cause is that the *velocity* with which the process of combustion is propagated in the explosive mixture, is much smaller in the case of the carbon monoxide and oxygen than of the hydrogen and oxygen mixture.

This velocity is greatly increased by the presence of a trace of water vapour. In the case of the carbon monoxide mixture which has been carefully dried with phosphorus pentoxide, the velocity is so small that it is not possible to bring about ignition by means of an electric spark; a mixture of perfectly dry carbon monoxide and oxygen appears to be incombustible in such a way. If, however, the mixture is heated from without, combination takes place.

* The same behaviour is evidenced by the fact that a jet of carbon monoxide burns in moist air with the well-known blue flame, but is extinguished when it is brought into dry oxygen, whereas it continues to burn in the moist gas.

* All these are *catalytic* actions. The assumption occasionally expressed that intermediate products are formed with the water, has not been proved; it may be right, but the mere assumption contributes nothing to the explanation of the phenomenon itself.

391. Water Gas. —The great advantages possessed by gaseous fuel with respect to completeness of combustion and power of regulating the flame, have given rise to many experiments to prepare a gaseous fuel, with as small a loss as possible, from the solid material, coal or lignite. A very promising reaction was found in the action of water vapour on charcoal, corresponding, according to circumstances, to one or other of the equations

$$C + H_2O = CO + H_2$$
$$C + 2H_2O = 2H_2 + CO_2$$
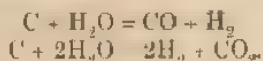
In the former case, charcoal and water vapour are converted into carbon monoxide and hydrogen, in the latter, into carbon dioxide and hydrogen. Of the two reactions, the former predominates at high

2 D

temperatures, while the second is favoured by a lowering of temperature.

Neither of the two reactions can take place spontaneously, for each is accompanied by an absorption of heat, amounting in the first case 133 kj, and in the second to 91 kj. The communication of necessary energy in some form must, therefore, be provided for. method consists in raising the coal to a high temperature by comtion with the help of an air blast, and then passing in steam the temperature has again sunk so low that the reaction would air is again injected, and the processes are repeated alternately these operations, care must be taken, by reversing the conduct tubes, that the mixture of carbon dioxide and nitrogen formed in heating process does not mix with the combustible gas formed another period of the process.

The second method consists in mixing the steam with as much as is necessary to maintain the temperature. The process is in way a continuous one, and therefore much simpler, but the gas duced has the disadvantage that it contains a fairly large amount carbon dioxide and nitrogen mixed with it, and therefore does allow of such high temperatures being attained as the pure "wat gas."

On account of the very poisonous nature of carbon monoxide, will always be better to aim at producing a gas which contains little carbon monoxide as possible and a correspondingly larger amount of hydrogen. This is the same as saying that the operations shou be carried out at as low a temperature as possible.

392. **Formic Acid.**—Carbon monoxide can be regarded as the anhydride of an acid which is called *formic acid* ($CO + H_2O = HCOOH$) because it was first observed in the acid liquid which ants squirt of for defensive purposes. Still, no appreciable amount of formic acid is formed when carbon monoxide and water are brought together The sodium salt, or *sodium formate*, however, is obtained when carbon monoxide is passed over gently heated caustic soda. The reaction $CO + NaOH = HCOONa$.

As is seen from the formula of the sodium salt, formic acid is a *monobasic* acid in spite of the fact that it contains two combining weights of hydrogen. One of these is not capable of being replaced by metals, the other, however, can be so very well. Formic acid can not even be called an acid of medium strength, although it approaches very near to one.

Free formic acid can be easily obtained by the distillation of the sodium salt with sulphuric acid. It is rather difficult to remove the last traces of water from it, since it readily decomposes again into water and carbon monoxide. It is best effected by allowing the fairly concentrated acid to partially solidify; an anhydrous acid then crystallises out and a more watery mother liquor remains. Pure

formic acid melts at 8·6 ; at the ordinary temperature it is a colour-less liquid with corrosive smell and action, which dissolves in water in all proportions and reacts strongly acid. With bases or metals, it forms salts which are mostly easily soluble in water and contain the colourless *formanion* HCO_2' ; by oxidising agents, it is readily oxidised to carbon dioxide : $HCOOH + O = CO_2 + H_2O$. It acts, therefore, with respect to some substances, as a reducing agent, and it precipi-tates, more especially, the noble metals such as gold and platinum, but also silver and mercury, from their salts.

Formic acid is usually classed with the organic acids because it is the first member of a large series of similar acids which differ from it in the fact that the non-ionisable hydrogen is replaced by the atomic group C_nH_{2n+1} (n being a whole number) ; in the simplest case, there-fore, by CH_3. The acid which is formed from formic acid by the introduction of CH_3 in place of hydrogen, is called *acetic acid* ; it has the composition $CH_3COOH = HC_2O_2H_3$, and is monobasic like formic acid. Since acetic acid is readily formed from organic substances, it is one of the longest known acids, and in most languages it has given the name to the group of the acids.

393. **Acetic Acid** has similar properties to formic acid ; it does not, however, exhibit the reducing actions of the latter, but is exceed-ingly stable towards oxidising agents. It is a colourless liquid which solidifies (when supercooling is avoided) at 17·5 , and which, on account of the ice-like appearance of the crystals, is called *glacial acetic acid*. It mixes with water in all proportions, yielding solutions of an acid taste. A solution containing about 3 per cent of acetic acid is used for household purposes under the name vinegar. In the labora-tory also, acetic acid is often used in cases where it is necessary to have an acid which is much weaker than the mineral acids, hydro-chloric or sulphuric acid, but which has nevertheless a distinct acid character and does not readily yield to other chemical attacks. Its salts, the *acetates*, contain the colourless *acetanion*, $H_3C_2O_2'$.

394. **Hydrogen Compounds of Carbon.**—The number of com-pounds which carbon forms with hydrogen is exceedingly great. The treatment of these belongs to organic chemistry, and only a few of the most important of the compounds of this group will be mentioned here, and their relations to the other simple carbon compounds discussed.

The simplest of all the substances of this group is the compound CH_4, which, from its occurrence, goes by the name of *marsh gas* or *fire-damp*, its systematic name is *methane*. It is a component of the gases which are evolved from decaying vegetation at the bottom of stagnant waters. The gas is also frequently found in coal mines ; it generally occurs shut up in cavities under some pressure, and escapes when these are opened in the mining. The name methane is derived from the relation which the gas bears to *methyl alcohol* (*vide infra*) wood spirit.

and is called *methyl*.   It does not exist alone any more than hydroxyl does; but as a constituent in organic compounds it plays a very important part.

This follows from the fact, discovered empirically, that those compounds in organic chemistry which may be regarded as being formed by the replacement of hydrogen by methyl, possess a very great *resemblance* to the parent compound.   An example of this we have already met with in the case of formic and acetic acids   If we compare the two formulæ HCOOH and CH_3COOH, which represent these two acids, we see that, as a matter of fact, acetic acid can be derived from formic acid by imagining the first hydrogen of its formula replaced by methyl.

Such a method of derivation can be employed in the case of all organic compounds containing hydrogen.   This can, in the first instance, be done for methane itself, and, in this way, there is obtained from methane CH_4 the compound $CH_3 . CH_3$, which is called *ethane*.   In this compound, the same change can be carried out, and we obtain *propane*, $CH_3 . CH_2 . CH_3$.   Evidently, there is no theoretical limit to this substitution, and, indeed, hydrocarbons of this kind are known up to C_{40} and over.   *Petroleum* consists of hydrocarbons of this class.

On writing the summed formulæ of these hydrocarbons, we obtain the series CH_4, C_2H_6, C_3H_8, C_4H_{10}, and so on.   Each successive hydrocarbon differs from the previous one by CH_2, one hydrogen being eliminated each time and CH_3 introduced instead.   Such a series of similar compounds which can be derived from one another by the substitution of methyl for hydrogen, is called an *homologous series*.

Besides the homologous series of the hydrocarbons, there is one of the *alcohols*, the *acids*, the *chlorides*, etc.

Of the homologues of the above mentioned substances, we may mention *ethyl alcohol*, homologous to methyl alcohol, which is known under the name of *spirit of wine*, *alcohol*, or *spirit*.   It has the composition CH_3CH_2OH or C_2H_6O, and can be derived from methyl alcohol by imagining one combining weight of hydrogen replaced by methyl.

Ethyl alcohol is prepared in very large quantities by the fermentation of sugar and substances containing sugar.   These have the composition $C_6H_{12}O_6$, and decompose, under the influence of a catalytic agent, *zymase*, which is secreted by various organisms, especially by yeast, into alcohol and carbon dioxide, according to the equation $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$.   The latter escapes, and from the aqueous mixture the ethyl alcohol is separated in the pure state by distillation.   It boils at 78°.

Ethyl alcohol is a colourless liquid with a feeble smell and burning taste.   For the organism it is, when concentrated, an acute, when diluted, a slow poison.   The phenomena of incipient poisoning become

the process of salt formation, in which hydrogen is also substituted. Whereas in the case of the acids, by no means all the hydrogen can be replaced, in the case of organic compounds, all the hydrogen can be substituted. Further, whereas the acid hydrogen can be replaced only by metals or metal like groups, the hydrogen of organic compounds can be replaced by the most different elements or groups. Finally, the compounds which are formed in the case of the organic substances are not salts, but undissociable or indifferent compounds. It is, of course, not excluded that organic substances may also yield acids, bases, and salts, but the formation and transformation of these follow the same laws as in inorganic chemistry. With the organic compounds, both kinds of processes, salt formation and substitution, may occur, correspondingly different substances being produced.

Thus, for example, the following compounds are successively obtained by the action of chlorine on methane (under the influence of sunlight) :—

Methyl chloride	CH_3Cl
Methylene chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Tetrachlormethane	CCl_4

All these substances are formed from methane, the hydrogen being replaced step by step by chlorine. Further, all are indifferent or non-saline substances. Their properties change gradually with the increase in the amount of chlorine, as is shown in the following table :—

	Density.	Boiling point.
Methyl chloride . .	0·9523	− 23·7°
Methylene chloride . .	1·3778	+ 41·6°
Chloroform . . .	1·5264	61·2°
Tetrachlormethane .	1·6320	76·7°

All these substances are only slightly soluble in water. The solutions do not exhibit any of the reactions of chloridion, *i.e.* on addition of silver nitrate they remain clear. Also, neither the solutions nor the pure substances possess the property of conducting the electric current.

The derivatives of methane containing bromine or iodine in place of hydrogen, are perfectly similar ; their properties also undergo a gradual change with increase in the amount of halogen. On the other hand, if the corresponding chlorine, bromine, and iodine compounds are arranged in a series, a similar gradation of properties is observed. This is shown, for the densities, in the following table :—

	Chlorine.	Bromine.	Iodine.
Simple substitution .	0·952	1·664	2·199
Double ,, .	1·378	2·994	3·342
Triple ,, . .	1·526	2·900	4·008
Quadruple ,, .	1·632	.	4·32

With fluorine also, corresponding compounds CF_4, CF_3H, CF_2H_2 are known. The general method of preparing these is by the interaction of the chloro-compounds on silver fluoride. *Carbon tetrafluoride* is also obtained by passing fluorine over porous charcoal at a low temperature. The gas, the density of which corresponds to the formula CF_4, condenses to a liquid at -15 under atmospheric pressure. It is difficultly soluble in water, but very readily soluble in ether and in anhydrous alcohol. It reacts with glass with formation of CO_2 and SiF_4. The above compounds are also readily formed by the action of gaseous fluorine on carbon compounds.

396. **Radicles.** Considering the compounds just described, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, we can formally regard the latter as chlorides of the groups CH_3, CH_2, CH, and C. Of these, the first is combined with one, the second with two, the third with three, and the fourth with four combining weights of chlorine. Just as we called a metal which can combine with two combining weights of chlorine, divalent, so we may call the group CH_2 divalent, and CH trivalent; in this sense, carbon is tetravalent.

It is a remarkable fact that hydrogen and the halogens do not form any other compounds with carbon, containing only one combining weight of this element, than the ones mentioned. In other words, in all these compounds carbon is *tetravalent*, for the number of the combining weights of hydrogen and the halogens together, is always equal to four.

On the other hand, the group CH_3 can be regarded as monovalent, because it can combine with still one combining weight of hydrogen or halogen; alone, it is incapable of existing. Likewise, the group CH_2 is divalent, and so on.

The monovalent group CH_3 is called *methyl*, the divalent CH_2 *methylene*, the trivalent CH *methenyl*.

Of these groups or radicles, the first is the most important, for it forms by far the most derivatives. Such compounds are formed not only by the replacement of hydrogen by other elements, such as the halogens, but, instead of elements, monovalent *radicles*, such as hydroxyl or amidogen, may replace hydrogen and give rise to corresponding compounds. The number of such radicles is very great, for every existing compound can, by the loss of one combining weight of hydrogen or another element, pass into a monovalent radicle.

397. **Methyl Alcohol.**—Of these compounds, one of the most important is that with hydroxyl, CH_3OH, which is called *methyl alcohol*. Formerly, the name alcohol was used to designate only spirit of wine, the volatile constituent of intoxicating beverages. It afterwards became a class name, and the hydroxyl compounds of the hydrocarbon radicles generally are called by the name alcohol.

Methyl alcohol is formed, along with many other volatile substances, by the *dry distillation*, i.e. by the heating, of wood. It is

...rated from the mixture by fractional distillation, and in the pure ... is a colourless liquid with a feeble odour and having the density ... It is combustible and dissolves in water in all proportions. ...boiling point is 66°.

Methyl alcohol is a type of the *alcohols*. These are indifferent ...ids, reacting neither acid nor alkaline with vegetable colours, whose ...eous solutions do not appreciably conduct the electric current, and ...ch are therefore not dissociated into ions. The alcohols can be ...ed with acids without immediate combination taking place. If ... two substances, however, remain mixed for a lengthened period, ...reaction slowly occurs, the course of which is quite similar to that ... salt formation. Thus, from methyl alcohol and hydrochloric acid, ...thyl chloride (p. 405) and water are formed, and the corresponding ...ation of reaction, $CH_3(OH) + HCl = CH_3Cl + H_2O$, has an appear ...ce quite similar to that of a salt formation, the methyl, CH_3, playing ... part of a cation.

However, the product of the action, the methyl chloride, is no salt ... the ordinary sense. As is seen from the statement of its properties ...ven on p. 405, it is, at the ordinary temperature, a gas which is con-...verted into a colourless liquid only at $-23·7$. Its aqueous solution ...es not conduct the electric current at all, and on the addition of ...ver solution, no precipitate of silver chloride is formed, so that no ...demonstrable amount of chloridion is present.

If, however, the silver solution is left very long in contact with ...methyl chloride, silver chloride begins to slowly separate out. One is, ...erefore, led to suppose that chloridion is indeed present in the ...queous solution, but in exceedingly slight amount. By the long ...ntinued action of the silver solution the amount of chloridion is ...en so far increased that silver chloride can be precipitated.

In fact, the most appropriate view of this kind of compound is ...hat besides the outward similarity between the alcohols and the ...ses and between their acid compounds and the salts, there exists an ...ner resemblance which is masked by the following circumstances. ...rst, the dissociation of these substances into ions is so exceedingly ...all that it cannot be detected by the ordinary means. Secondly, ...e processes of dissociation into and recombination of the ions takes ...ace disproportionately slower in the case of these substances (chiefly ...bably reason of the extraordinarily small concentration of their ions) ...han in the case of the typical bases and salts. It is suitable, there-...fore, not only to retain the name alcohol for the hydroxyl compounds, ...but also to call their acid derivatives not salts, but to introduce a ...pecial name for them. They are called *esters*. Methyl chloride is, ...therefore, the hydrochloric acid ester of methyl alcohol.

The Radicle Methyl and Homologous Series.—From ...thane, CH_4, which is a "saturated" compound, there is formed, by ...oss of hydrogen, a monovalent radicle which has the composition CH_3,

so the higher the pressure, acetylene becomes an explosive substance, undergoing decomposition with great violence when decomposition is started by any means at some point. The same property is exhibited by *liquid* acetylene. Since the critical temperature of this gas is 37°, and the critical pressure 68 atm., the liquefaction of the gas can be easily accomplished. This operation is without any great danger when carried out at low temperatures, in which case only slight pressure has to be applied; but at higher temperatures, with correspondingly greater pressures, it becomes on the whole very dangerous, and has claimed several victims.

Connected with the great absorption of energy in the formation of acetylene from its elements is the fact that it is formed from the latter at very high temperatures (p. 331). For example, if an electric current be allowed to pass between two carbon poles in a space in which hydrogen is present (Fig. 111), the latter combines with the carbon with formation of acetylene.

The detection of acetylene depends on its power of yielding precipitates with a solution of a silver salt, or of a *silver salt* in excess of ammonia, these precipitates being the carbon compounds or acetylides of the respective metals. The silver precipitate is white, the copper one red. In the dry condition both explode violently; on being treated with acids they again yield up the acetylene.

4. Coal Gas.—The combustible gas which is used for heating and illuminating purposes, and which, under the name of *coal gas,*

gas tar is a mixture of hydrocarbons and their derivatives. It is the source for obtaining *benzene, naphthalene*, and *anthracene* hydrocarbons which are of the greatest importance for the preparation of artificial dye stuffs and medicaments; from it there are also derived *phenol (carbolic acid)* and compounds related to it, which are used for purposes of disinfection and for the preparation of smokeless powder. Numerous other substances are present in gas tar, and are used as crude material, so that it may be designated as the most important starting substance in the *industrial chemistry of the organic compounds*.

The working up of the gas tar is also carried out essentially by fractional distillation, with the aid of lime and sulphuric acid. The details of this belong to the chemical technology of the organic compounds.

The gas, which is evolved at the same time, is freed by cooling and washing from the tar; and by passing it over a mixture of lime and oxide of iron, the sulphur compounds it contains, and which, by reason of the formation of sulphur dioxide would have a baneful effect when the gas is used in inhabited rooms, are removed; it is then stored in large gas holders for distribution through the network of tubes to the individual consumers.

Coal gas varies considerably in composition, according to the coal used for its preparation. Its chief constituents are hydrogen, methane, carbon monoxide, and some hydrocarbons richer in carbon, namely ethylene, benzene, and naphthalene. The latter two compounds are respectively liquid and solid at the ordinary temperature; they can mix with the gas, therefore, only in amount corresponding to their vapour pressure, and again separate out when the gas experiences a considerable lowering of temperature.

To give an idea of the composition of ordinary coal gas, we give the results of an analysis in which the constituents are stated in *per cent. by volume:*—

Hydrogen	.	.	.	49·6
Methane	.	.	.	29·8
Carbon monoxide	.	.	.	9·6
Hydrocarbons	.	.	.	5·0
Carbon dioxide	.	.	.	2·7
Nitrogen	.	.	.	2·6
Benzene vapour	.	.	.	0·7

The "hydrocarbons" consist chiefly of ethylene.

At first coal gas was chiefly prepared for illuminating purposes, and the chief attention was therefore directed to obtaining a gas rich in ethylene and other "heavy hydrocarbons." Such can be obtained only from certain expensive kinds of coal, and the product, therefore, coal gas, is correspondingly dearer. Meanwhile, the gas has been found to be very convenient for heating purposes and for driv-

The flame of a Bunsen burner consists of two parts: an inner, an hollow cone, and an outer, blue mantle. In the hollow cone combustion of the hydrogen and of the carbon to carbon
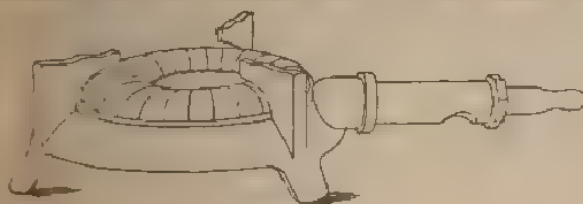

Fig. 104.

oxide essentially occurs; in the outer mantle the combustion dioxide is completed. For this reason, the inner cone has a reducing action on substances introduced into it, whereas in the outer of the mantle an excess of oxygen is present. These differences made use of for the purposes of chemical analysis.

For this purpose, besides the *inner* cone, *a, a, aa* (Fig. 105) and the mantle, *a, a, c,* Bunsen distinguished the *luminous tip, aba,* which produced when the air holes of the burner are partially closed. It not present in the normal Bunsen flame. In these three portions are six reaction spaces, namely, the *basis* of the flame *a,* which is coldest part of the flame ; the *fusing* space, β, which is the hottest ; γ is the *lower,* and ϵ the *upper oxidising flame ;* while δ is the and η the *upper reducing flame.* The former acts less vigorously, unconsumed air is still present, but it is hotter than the upper flame which contains an excess of reducing carbon.

Oxalic Acid.—By the oxidation of many carbon compounds are is formed an acid of the composition $H_2C_2O_4$, which, by reason of manifold importance, we shall also mention here. It is called *oxalic* and since both its hydrogens are replaceable by metals, it is a basic acid.

Oxalic acid is a white crystalline substance, which readily dissolves water, and gives an acid reaction ; it is found to be an acid of medium strength. The ordinary crystallised oxalic acid contains of crystallisation, and its composition is represented by the formula $H_2C_2O_4 \cdot 2H_2O$. With bases it forms two series of salts, acid and normal, and most of these are difficultly soluble in water. Of these the most important are the acid potassium salt and the normal potassium salt.

The former, having the composition KHC_2O_4, occurs in many plants possessing an acid taste, and can be obtained crystalline by the evaporation of the juice pressed out from these. For its preparation was formerly chiefly used the wood-sorrel (*oxalis*), from which name oxalic acid is derived ; likewise, the potassium salt is called of sorrel.

The neutral calcium salt CaC_2O_4 is very difficultly sol
water. It occurs in almost all plants, being found in the
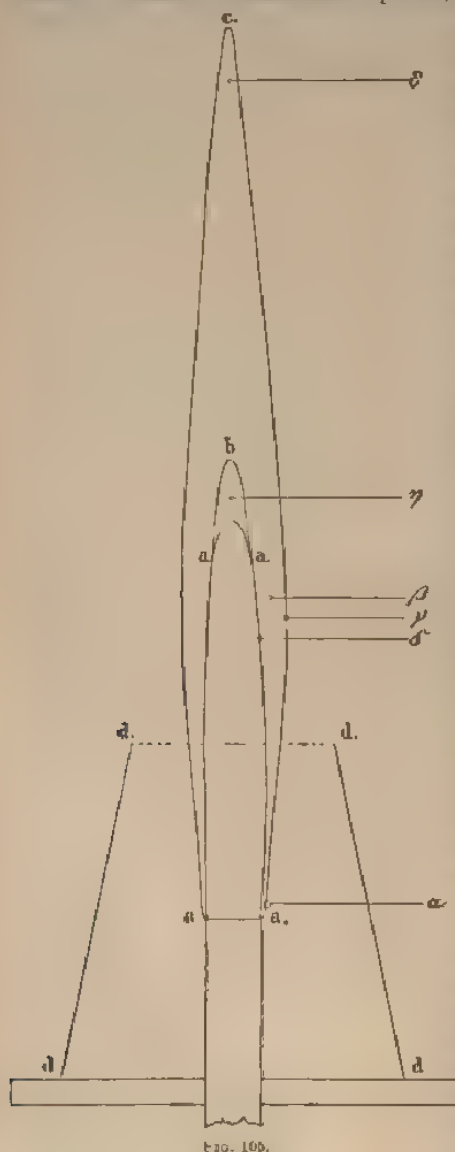
very characteristic h
crystals which have
pearance of envelop
analytical chemistry
importance from the f
it is the form in wh
calcium compounds
tected qualitatively
termined quantitativ
reagent for this purp
ammonium salt of ox
is mostly used.

On being heated
acid first decompose
formic acid and car
oxide, $H_2C_2O_4 - HC$
CO_2, but this decom
can be accomplished
with great care or w
help of suitable cat
On heating more a
the formic acid also
poses, and there are o
carbon dioxide, carbo
oxide, and water: H
$CO_2 - CO + H_2O$. T
of oxalic acid on being
are converted, with o
of carbon monoxid
carbonates, which i
cases decompose
e.g. $CaC_2O_4 = CaCO_3$
$CaO + CO_2 + CO$.

Further, oxalic a
composes into carbo
oxide and carbon
when treated with d
ing agents, such as
trated sulphuric acid
reaction is made u
the convenient prep
of carbon monoxide

Fig. 105.

acid or a salt of this is warmed with concentrated sulphuric a
the escaping gases passed through a wash-bottle with caust

The carbon dioxide is absorbed by this, and pure carbon monoxide is obtained.

Oxalic acid is fairly sensitive to oxidising agents, and is readily oxidised by them to carbon dioxide: $H_2C_2O_4 + O = 2CO_2 + H_2O$. This reaction is also used in analytical chemistry, and we shall later have occasion to return to it (Chap. XXVIII.).

403. **Carbon Disulphide.**—When charcoal is heated in a current of sulphur vapour, a compound of the two elements is formed. It has the composition CS_2, for its vapour density is 76, and analysis shows it to contain 64 of sulphur to 12 of carbon.

Carbon disulphide is a colourless liquid, whose density is about 1·3, and which boils at 47°. In the pure state it is almost colourless. Ordinary carbon disulphide, owing to the presence of other sulphur compounds, has generally rather a bad smell. It can be purified by shaking with metallic mercury and distilling.

Carbon disulphide refracts and disperses light very strongly, its indices of refraction (at 17·00°), for the most important rays, are :—

	A	B	C	D
Wave-length	7604	6867	6562	5890×10^{-8} cm.
Index of refraction	1·61136	1·61756	1·62086	1·63034

	E	F	G	H
Wave-length	5270	4861	4308	3968×10^{-8} cm
Index of refraction	1·64120	1·65529	1·67975	1·70277

For this reason it has often been attempted to use it for optical apparatus, e.g. for prisms in spectroscopes. This, however, has not met with success, since the great expansion by heat very readily causes disturbances; further, carbon disulphide is somewhat sensitive to light, and when exposed to light for a lengthened period it decomposes and its properties change.

Carbon disulphide is a good solvent for many substances; in this rôle we have already met with it in the case of sulphur and iodine. It also readily dissolves fats and resins, a fact on which many technical applications of it depend.

By reason of being composed of two combustible elements, carbon disulphide can be ignited, and it burns in the air with a blue flame, with formation of sulphur dioxide and carbon dioxide. Its *temperature of ignition* is very low, so that the vapour of carbon disulphide can be ignited under circumstances in which other combustible substance far from taking fire. Corresponding care must, therefore, be of in using this compound.

Mixed with nitrous oxide, carbon disulphide burns with a which is especially rich in ultraviolet and violet rays, and which fore, under certain circumstances, is used for photochemical pu The sulphur dioxide thereby formed, however, is a hindrance general use.

2 E

Carbon disulphide is formed from its elements with absorption of 120 kj. Its heat of combustion amounts to 1320 kj, whereas that of the elements is only 1200 kj. In very special circumstances, therefore, it may be caused to decompose explosively; this, however, is difficult, and, as a rule, it exhibits no explosive properties.

From carbon disulphide an acid is derived which bears the same relation to it as carbonic acid does to carbon dioxide. Only, this acid is not composed of carbon disulphide and *water*, but of carbon disulphide plus *sulphuretted hydrogen*, and has, therefore, the composition H_2CS_3.

From this example it will be seen that besides the oxyacids there are others which have a similar composition to these but contain sulphur in the place of oxygen. These are called *thio-acids*, and the above acid, *thiocarbonic acid*, is such an acid, as can be seen by writing the two formulæ side by side : —

Anhydride	CO_2	CS_2
Acid	H_2CO_3	H_2CS_3
Sodium salt	Na_2CO_3	Na_2CS_3

The sodium salt of *thiocarbonic* is obtained by dissolving carbon disulphide in a solution of sodium sulphide, in accordance with the equation $CS_2 + Na_2S = Na_2CS_3$. From a solution of this salt, the carbonic acid can be precipitated by addition of an acid. Like carbonic acid, it only slowly decomposes, so that it separates out as an oily liquid, only slightly soluble in water. This is, however, not stable, but slowly decomposes into carbon disulphide and sulphuretted hydrogen : $H_2CS_3 = H_2S + CS_2$.

The thiocarbonates have attained to a certain importance from the fact that carbon disulphide has been found to be a means for destroying the phylloxera. Whereas carbon disulphide is so volatile as to be inapplicable for this purpose, the thiocarbonates are suitable.

Under the influence of the carbon dioxide in the air and in the soil, these are converted into carbonates, carbon disulphide and sulphuretted hydrogen being split off : $Na_2CS_3 + CO_2 + H_2O = Na_2CO_3 + H_2S + CS_2$. The process takes place slowly, but still with such rapidity that the amount of carbon disulphide present at each moment is sufficient to exercise the desired action.

The existence also of a compound CS has recently been rendered very probable. It was obtained as a colourless gas, by heating copper in the vapour of carbon disulphide diluted with nitrogen, according to the equation : $CS_2 + Cu = CS + CuS$.

404. Carbon Oxysulphide.—In various ways, most easily by the decomposition of the thiocyanates (*vide infra*) with sulphuric acid, a compound, COS, is formed which can be regarded as an intermediate compound between carbon dioxide and carbon disulphide. It is a gas which is readily absorbed by water, with which it slowly interacts, with

...tion of carbonic acid and sulphuretted hydrogen: $COS + 2H_2O =$ ... H_2S. This reaction is greatly accelerated by the addition of ..., the salts of the two acids being formed.

Carbon oxysulphide smells somewhat like sulphuretted hydrogen, ... readily burns in the air with a blue flame, forming carbon dioxide ... sulphur dioxide.

Cyanogen. When carbon and nitrogen are exposed to very ... temperatures, such as exist, for example, in the electric arc (Fig. ..., p. 4121, these two elements combine to form a gas which, in ... with its composition and density, 52, has the formula ... On account of the blue compounds which it yields with iron, ... which have been known for long, this substance has received the ... (producer of blue substance).

Cyanogen is a colourless gas with peculiar smell and poisonous ... on the organism. Its critical temperature is 124, its critical ... 62 atm. In its solubility in water it resembles carbon ..., to which it also approximates with respect to its density ... as compared with 44)

Cyanogen can be ignited in the air, and burns, with a characteristic ... of red violet colour, to carbon dioxide and nitrogen. A consider... amount of heat is thereby developed, amounting to more than ... be given by the corresponding amount of charcoal. Cyanogen, ... also belongs to those compounds which are formed with ... of energy, and whose spontaneous formation occurs at very ... temperatures. It is thus formed on all occasions where carbon ... nitrogen come together at a high temperature, e.g. in the blast ... in the preparation of iron. The heat of combustion of ... is 1087 kj, whereas that of two carbons amounts to 812 kj, ... formation of the gas, therefore, 275 kj are absorbed.

In its chemical relations, cyanogen is analogous to the *halogens*, ... has a whole series of compounds in which the group CN behaves ... chlorine or iodine. More especially, it forms with the metals, ..., which contain the colourless, highly poisonous monovalent ... ion CN'.

... the first place, there should be mentioned the hydrogen com... HCN, *hydrocyanic acid* or *prussic acid*. This compound is ... by decomposing the metallic cyanides with an acid, just as ... hydrochloric acid is obtained from common salt. The metallic cyanides, ... in, are formed by allowing carbon nitrogen, and the respective ... or their carbonates, to act on one another at a high tempera... A more exact description of what takes place here will be ... later under the metals.

For the liberation of hydrocyanic acid from its salts, a strong acid ... required, for hydrocyanic acid stands at the outermost limit of ... weak acids. The aqueous solution scarcely exhibits an acid ..., and dissolved metallic cyanides can be decomposed even by

such weak acids as carbonic acid.   In consequence of this the me
cyanides, when exposed to the air (containing carbonic acid), sui
hydrocyanic acid, and the aqueous solutions are partially diss
hydrolytically and react alkaline (p. 250).

In the pure state, hydrocyanic acid is a colourless liquid
boils at 27 and solidifies at -15 .   It is a highly poisonous
pound, which even in small amounts quickly acts fatally.   The
of its poisonous action is probably due to its being a retarding cat
for many physiologically important processes, especially the oxid
in the organism.

Hydrocyanic acid can be detected even in small quantities
smell, which recalls that of bitter almonds.   The reason of this i
in bitter almonds a substance, amygdalin, is present which decom
under the influence of a catalyser or enzyme, which is also pres
other cells, into hydrocyanic acid, sugar, and a volatile oil
bitter almonds.   Crushed bitter almonds, therefore, smell of h
cyanic acid when, owing to the destruction of the cells, these
substances, amygdalin and the enzyme, come together.

Whereas the aqueous solution of hydrocyanic acid contains ex
ingly few ions, the soluble metallic compounds, which, in a corresp
ing manner to the chlorides, are obtained by the action of hydroc
acid on the oxides or hydroxides of the metals, are normally disso
into their ions.   Thus, the solution of one of the best known me
cyanides, potassium cyanide, KCN, contains the ions K' and
The ion CN' has a great resemblance to the ions of the halog
with argention, for example, it gives a difficultly soluble compo
which is deposited as a white precipitate, very similar to
chloride, when cyanidion and argention (e.g. from potassium cy
and silver nitrate) are brought together in solution.

* For the purpose of detecting cyanogen compounds, use is
of various very sensitive reactions, which may be shortly menti
here, although their theory cannot be given till later (Chap. XX
The liquid to be investigated, after being made alkaline by additi
caustic soda or potash, is warmed with a mixture of ferrous and f
salts, and hydrochloric acid then added.   If cyanidion was prese
dark blue precipitate is obtained, or, in the case of very small qu
ties, a blue or green-blue coloration.   The blue iron compou
hereby formed which has given the name to the whole group.

* Or, the liquid, with addition of yellow ammonium sulphid
evaporated to dryness, the residue dissolved in a drop of water
ferric chloride added.   If cyanidion was present, a blood-red co
tion is produced.   This depends on the formation of *thiocyanic*
means of the sulphur from the ammonium sulphide, and this give
above reaction with ferric chloride.   A knowledge of this test
practical importance by reason of the not infrequent cases of pois
with prussic acid, or with cyanides.

Relation of the Cyanogen Compounds to the Ammonia ... atives of the Carbon Compounds.—When hydrocyanic acid ... with strong hydrochloric acid, a reaction takes place, and ... chloride and formic acid are produced. The reaction can ... upon as essentially a taking up of water. hydrocyanic acid ... water yield formic acid and ammonia, in accordance with the ... $HCN + 2H_2O = HCOOH + NH_3$.

... reaction recalls the conversion of the amides into the ... salts of the corresponding acids (p. 346), but it differs ... by the fact that *two* moles of water are taken up instead of ... In suitable cases, therefore, there are two stages of dehydration ... ammonium salts the first yields the amide, the second a ... for which the general name *nitrile* has come into use. In ... case we have

Ammonium formate	$HCOO \cdot NH_4$
Amide of formic acid, or formamide	$HCO \cdot NH_2$
Nitrile of formic acid, or hydrocyanic acid	HCN

... matter of fact, hydrocyanic acid can be obtained from ... formate by means of strongly dehydrating agents.
... series shows cyanogen itself to be the nitrile of oxalic

Ammonium oxalate	$C_2O_4 \cdot NH_{4,2}$
Amide of oxalic acid, or oxamide	$C_2O_2 \cdot NH_{2,2}$
Nitrile of oxalic acid, or cyanogen	C_2N_2

... also, we may pass through the series not only by dehydra ... above downwards, but also by absorption of water from ... upwards.
... further extension of these indications belongs to organic ...

Cyanic Acid.—Of the oxyacids of cyanogen which would ... to the acids from hypochlorous up to perchloric acid, only ... member is known. By analogy, this should be called hypo ... acid, since its composition is represented by the formula ... since, however, no other oxygen compound is known, it is ... *... acid.*

... acid is a very unstable compound. It is obtained by ... another compound, *cyanuric acid*, which has the same composi ... but three times the molar weight, $H_3O_3C_3N_3$. From the vapour ... substance there is deposited, in accordance with the law of the ... of the unstable forms, not the stable cyanuric acid but the ... *... acid*, $HOCN$. The condensation of this compound, ... must be carried out at as low a temperature as possible, for, ... heating, cyanic acid is converted, with strong development ... sometimes with explosive violence, into more stable forms, of ... there are several. It is a colourless liquid with a strong smell, ... that of acetic acid.

In aqueous solution, also, cyanic acid is not stable, but is quickly converted, by absorption of water, into acid ammonium carbonate. This process is represented by the following equation: $HOCN + 2H_2O = (NH_4)HCO_3$. For this reason, a solution of a cyanate on being acidified effervesces and evolves carbon dioxide as if a carbonate were present. After the reaction, an ammonium salt is present in the solution.

Although cyanic acid is very unstable, i.e. cyananion, CNO, can exist, along with hydrion in equilibrium, the salts of cyananion, the cyanates, are mostly very stable compounds. They are formed, for example, with great readiness by exposing the cyanides to the action of oxidising agents. On this account, fused potassium cyanide is a powerful reducing agent, which withdraws the oxygen from various metallic oxides and converts them into metals. This reduction can be shown with especial ease in the case of lead oxide and bismuth oxide; under the liquid salt, the metals fuse together into drops which look bright like mercury. The same reaction is made use of for obtaining cyanates, especially potassium cyanate, from the corresponding cyanides; as oxide, pyrolusite (p. 55), is mostly employed.

A specially interesting reaction of cyanic acid is the transformation which its ammonium salt undergoes, and which led to the synthesis of urea (p. 398).

Ammonium cyanate has the formula NH_4OCN, and contains the same elements in the same proportions as urea, for both have the total formula CH_4N_2O. If, however, it is attempted to prepare ammonium cyanate, urea is obtained in its place. In the meantime, however, it has been shown that true ammonium cyanate possessing the expected properties of this substance exists; but it is very unstable, and rapidly undergoes transformation into the isomeric compound urea.

This reaction takes place so soon as the ions OCN′ and NH₄˙ come together in aqueous solution. On mixing any cyanate, e.g. potassium cyanate, and an ammonium salt, e.g. ammonium sulphate, in aqueous solution and evaporating the solution, a residue of potassium sulphate and urea is obtained, which can be readily separated by means of alcohol.

* Conversely, a small amount of ammonium cyanate is formed in an aqueous solution of urea, especially on heating, so that a chemical equilibrium is established between the two isomeric substances as a result of their mutual convertibility.

108. Thiocyanogen.—If potassium cyanide or other cyanide is fused with sulphur or a sulphur compound, or even if a solution of one of these salts is heated with sulphur, the latter is taken up and a solution of a salt is obtained of the composition MSCN, in the case of potassium, therefore, KSCN. This compound, which gives a very pronounced blood-red or brown-red coloration with ferric salts,

called *potassium thiocyanate*, it is the potassium salt of thiocyananion, SCN.

The composition of these compounds is similar to that of the cyanic acid compounds, only that sulphur is present in the place of oxygen. *Thiocyanic acid* is distinguished from cyanic acid by its much greater stability.

From the barium salt, by precipitation with sulphuric acid (p. 293), an aqueous solution of thiocyanic acid can be obtained; this is a very acid liquid whose acid properties are not greatly inferior to those of hydrochloric acid. In the free state, thiocyanic acid is unknown; on attempting to prepare it, a rather complex decomposition occurs in which carbon oxysulphide, COS, is formed (p. 418). The formation of this latter compound takes place directly by splitting off ammonia with the aid of water, a reaction which can be represented by the equation $HSCN + H_2O = COS + NH_3$. The decomposition occurs on heating potassium thiocyanate with a medium strong solution of sulphuric acid.

With regard to its similarity to the halogens, thiocyananion, SCN, is quite analogous to cyananion; it, also, gives with argention a white precipitate, which, in its external appearance, cannot be distinguished from silver chloride or silver cyanide.

Corresponding to the *gaseous* cyanogen, however, no thiocyanogen is known. There are substances, it is true, which have the composition SCN, but these are certainly polymeric compounds of the formula SCN_n, where n is a number probably greater than 3. They belong, therefore, to quite a different group of substances, which are generally treated in organic chemistry.

CHAPTER XVII

409. General Silicon stands to carbon in the same relation as sulphur to oxygen. The two elements are similar in many respects, but differ more from one another than, for example, chlorine, bromine, and iodine do.

Silicon, like carbon, occurs in *several* forms, of which an *amorphous* and a *crystalline* form are accurately known. Amorphous silicon is obtained by conducting its chlorine or fluorine compound over heated potassium; the metal unites with the halogen, and the silicon is set free. The soluble potassium salt formed is removed by washing with water, and the silicon is left behind as a greenish-brown powder. This is amorphous, and has the tendency to pass into the colloidal state. If, therefore, the washing is continued to a certain point, the silicon goes into a sludge and begins to pass through the filter.

Amorphous silicon is more easily obtained by heating its oxygen compound, finely powdered quartz, with *magnesium powder*. The magnesium combines with the oxygen of the silicon dioxide, forming magnesium oxide, and the silicon is liberated. The latter can be obtained pure by extracting the product with dilute acid, in which the magnesium oxide but not the silicon dissolves.

At a high temperature, silicon melts, and on solidifying, crystalline silicon is formed as a grey mass with a metallic lustre. The crystallisation is greatly facilitated by the addition of a metal such as zinc; the zinc can be removed by treating the product with dilute acids.

Amorphous silicon can be set on fire in the air, but its combustion is very incomplete, because the non-volatile silicon dioxide formed prevents further combustion. *Crystalline silicon* does not noticeably change in the air even at a red heat. Silicon is soluble in caustic soda on heating, the silicon thereby taking up oxygen from the water and passing into an acid, silicic acid, or rather into its sodium salt. The hydrogen of the water escapes as a gas.

The combining weight of silicon has been determined by the analysis of its halogen compounds, and amounts to $Si = 28.4$.

Silicon Dioxide.—By far the most important compound of [si]licon dioxide or the *anhydride* of silicic acid. It has the [formula] SiO_2, or a multiple of this, and occurs in enormous quantities [...] both in the free state and as salts. The largest part of the [earth's?] surface is composed of silicon dioxide, or of its compounds; [a] quarter of the solid crust of the earth is formed by silicon [Silic]on dioxide occurs in several varieties, two crystalline and one [amorph]ous. It is most widely distributed in the crystalline form as [r]ock crystal, amethyst, smoky quartz. These and various [m]inerals are, chemically, the same substance, and appear to be [it] only by reason of the impurities to which the difference in [is] due.

[The] purest form is *rock crystal*, which crystallises in six sided [and] is colourless. The crystals possess the property of *rotating* [plane?] of polarised light when this is passed through parallel to the [axis of] the prism. In some crystals the rota[tion is] to the right, in others to the left, and the [...] the rotation is closely related to a one[sided] crystallographic formation, by means of [which] right and left crystals can also be dis[tinguish]ed. The difference is seen in the hemi[hedral] faces (Fig. 106); a right and a left [crystal] can no more be superposed on one [another] than can a right and a left hand glove.
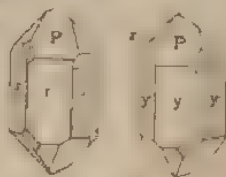
Fig. 106.

[Th]e rock crystal is clear as water, smoky topaz, or, better, [qu]artz, is brown to black, *amethyst* violet, ordinary *quartz* [grey] and turbid. There are also yellow, rose red, and other [coloured] varieties

[Quar]tz forms a constituent of many rocks, especially of granite, [etc.] By the action of water and carbonic acid, these rocks are [disintegr]ated as well as partially changed chemically (*vide infra*), and [quar]tz grains are left detached. These are borne away and [taken] up by the rivers, and finally reach the sea in the form of [sand] On the sea-bottom the sand masses frequently become [cemented] again by means of a binding material (limestone or iron oxide) [to] masses, *sandstone*, which forms extensive mountain ranges [consisting] of quartz grains, has been so formed

[Quar]tz has the density 2·66, and a hardness 7, *i.e.* it represents the [hard]est grade after the diamond. Quartz is used, therefore, for [working?] metal (grindstones and whetstones) and glass

[Anot]her crystalline form of silicon dioxide is called *tridymite*. It [occurs al]most solely in microscopic crystals as a constituent of rocks, [less] dense than quartz (2·3 as compared with 2·66)

[Amorph]ous silicon dioxide occurs as a mineral in various rocks. [The most] widespread and best known form is *flint*, which forms [the] masses in chalk, and is coloured by organic substances yellow,

brown, or black. It is but slightly inferior to quartz in hardness, a
by reason of its conchoidal fracture sharp edges can easily be form
on it. In prehistoric times, when the methods of obtaining and work
ing metals were unknown, this mineral was used for making kniv
axes, and arrow heads. It is the stone which was chiefly employ
in the "Stone Age"

Another form of amorphous silicon dioxide is opal. Chalcedony
jasper, etc., which were formerly regarded as amorphous, are "crypt
crystalline," *i.e.* are composed of very small crystals. *Kieselg*
(diatomaceous earth) is a fine powder consisting of the shells of de
organisms (diatoms, etc.). In chemical operations, silicon dioxide
usually obtained amorphous, and it is not very easy to cause it
crystallise; nevertheless, both crystalline forms have already be
artificially prepared.

The amorphous varieties readily dissolve in boiling caustic sol
with formation of salts, but the crystalline forms are scarcely attack

The melting point of silicon dioxide is so high that the latter
not melt in the ordinary fire, but does so in the oxyhydrogen flam
It then forms a viscous liquid which looks like fused glass, and ca
be blown. In recent years vessels have been made of this amorpho
"quartz glass." On account of their small coefficient of expansion
with heat, they can be subjected to sudden changes of temperatur
without cracking; they are also very resistant to chemical action

411. **Silicic Acid**. Silicon dioxide is the anhydride of an acid
silicic acid, or rather of a whole series of acids which can be com
pounded of the elements of silicon dioxide and water. The relation
are similar to those obtaining in the case of the phosphoric acids, on
more diverse.

As extreme member of the series of the different silicic acid
there may be regarded the tetrabasic orthosilicic acid, $Si(OH)_4$, SiO_2 +
$2H_2O = Si(OH)_4$. It is not known in the pure state, but in the for
of its salts.

By loss of water, it passes into the dibasic acid $SiO(OH)_2$, th
composition of which corresponds to that of carbonic acid

Other silicic acids are formed by the union of several combining
weights of the ortho acid with loss of water. From $2Si(OH)_4$ ther
are formed $Si_2O_7H_6$, $Si_2O_6H_4$, $Si_2O_5H_2$. In a similar manner, corre
sponding "pyro-acids" can be derived from several combining weight
of silicic acid

Unlike the phosphoric acids, the different silicic acids cannot b
distinguished from one another by any reactions; that these differer
types exist can be concluded only from the existence of the corre
sponding salts which occur naturally in the crystalline form

These salts of silicic acid or silicates are all practically insolub
in water, with the exception of the silicates of the alkali metal
which can be dissolved, and whose solutions bear the name of wa

These salts are readily obtained by fusing quartz with the oxides or carbonates of the alkali metals. From these solutions, silicic acid can be set free by other acids.

If the mixing of an alkaline silicate with acid, e.g. hydrochloric, be carried out in concentrated solution, the silicic acid separates in friable, gelatinous masses. If, however, dilute solutions are employed and an excess of acid, no precipitation is obtained, but the solution remains clear and apparently unchanged. This looks as if silicic acid were difficultly soluble, so that it is partially precipitated from concentrated solutions while it remains dissolved in much water. This is, however, not the case, the solution of silicic acid which is formed is no true solution, but the silicic acid is present in the colloidal state.

This is seen when the liquid is subjected to dialysis, i.e. when it is placed in a vessel whose walls are formed entirely or partially of parchment paper or of bladder, and the vessel placed in pure water. The salt which is formed and the excess of acid then pass by diffusion freely through the membrane, while the silicic acid, like all colloidal substances, is retained. If the experiment is continued for a number of days with frequent renewal of the water, all the salts, as far as can be detected, will finally diffuse away, and the solution in the vessel will contain only silicic acid.

This silicic acid shows the characteristic properties of "colloidal solutions" or "pseudo-solutions." On evaporating to dryness no crystals are formed, but there is left an amorphous, glassy mass which only incompletely re-dissolves in water. Boiling and freezing point differ only exceedingly slightly from those of water, special chemical reactions cannot be detected. By addition of various substances, especially of salts, the liquid solidifies to a jelly, especially if it has been somewhat concentrated by evaporation in the cold.

In nature silicic acid occurs very often in such a form. It gets into the natural waters from the silicates when these are decomposed by carbonic acid. Under suitable conditions, the silicic acid crystallises from such solutions; smoky quartz, especially, has probably been formed in this way. For, since it owes its coloration to organic substances which are destroyed by ignition, it must have been formed at a low temperature, and, during the period of its existence, can never have been subjected to a red heat. The way in which it occurs, also, makes its formation from solutions probable.

Silicic acid, or quartz, is extensively applied in the arts. Sandstone is a greatly valued building material, because of its being easily worked and resistant; quartz sand is used as an addition to mortar and for grinding. By fusing quartz with the carbonates of the alkali and alkaline earth metals, amorphous, transparent masses are obtained, which we shall see, find very manifold application. Colourless rock crystal is used as a cheap ornamental stone, and also, on account of its rotating

the plane of polarised light and of its transparency for light of all wave-lengths, in the construction of optical instruments. For spectral glasses, also, quartz is used, since, on account of its great hardness, it loses the polish less easily than glass lenses.

412. Geological Reactions.—Of all chemical processes occurring on the earth's surface, the interaction of the naturally occurring silicates with water and carbonic acid is the one which, quantitatively, stands pre-eminent. The primitive rocks of the earth were essentially silicates; the carbon, in all probability, was present as carbonic acid. This corresponds to the equilibrium at comparatively high temperatures, which must be assumed to have prevailed originally on the earth.

At lower temperatures the equilibrium changes in such a way that carbonic acid displaces silicic acid from its salts. In other words, a system consisting of *carbonates* and *free silicic acid*, or silicon dioxide, is, at lower temperatures, more stable than the system *carbon dioxide* and *silicate*. For this reason, the silicates of the various primitive rocks are subjected to uninterrupted chemical change, to which is added a mechanical disintegration by the action of water, of changing temperature, and of the wind. The consequence of this is that the silicates which are decomposable under these circumstances are transformed, the non-decomposable are disintegrated, and carbonates are formed from the constituents of the transformed rocks.

The silicates of the alkali metals, especially, undergo this decomposition. These, it is true, do not occur in the free state in nature, but only as double silicates combined with the silicates of other metals. They become thereby more stable, but still not absolutely resistant, and are therefore decomposed.

The ions of the alkali metals pass into the waters as soluble carbonates, and are partially retained in the soil by absorption. This retention is specially great in cultivated soil, where it is conditioned, partially at least, by the presence of organic substances. Another portion passes on into the sea. This is also the destination of the alkaline earth metals, which are there deposited chiefly as carbonates.

Of the dissolved silicic acid, a considerable portion also reaches the sea, and is there utilised by various animals for building up their skeletons. Another portion forms hydrated magnesium silicate with the magnesium of the rocks. This is a compound which, under certain circumstances, resists the action of water, and which is therefore formed when its constituents come together. The conversion of the original rocks into serpentine or steatite, as the hydrated silicate of magnesium is called in mineralogy, can constantly be recognised at various points.

Of the other metals which occur abundantly on the earth's surface, aluminium also is capable of remaining in combination with silicic acid, even under the existing conditions. *Aluminium silicate* is a very widely distributed constituent of the primitive rocks. In the decom-

on by water and carbonic acid, or "weathering," aluminium
 is not decomposed, but remains as an amorphous or crypto-
alline residue when the other constituents have been dissolved.
very finely divided mass is carried by the rivers to the sea if it
 previously been deposited at comparatively quiet spots as *clay*,
 earth, or *loam*. On the sea bottom the deposited clay slowly
 into slate and similar secondary rocks.[1]

 means of these various transformations, a one-sided change
 place in the composition of the earth's crust, the tendency of
 is to more and more increase the amount of carbon in the form
 lime and magnesium carbonate, while the silicic acid which
 had formed salts with these metals is separated in the free

By this process the amount of carbon dioxide in the air must
 lowly become less. By the combustion of fossil fuel, it is true, a
 amount of the carbon which had been long removed from the
 again given back to it, and in isolated localities where volcanic
 occurs at a comparatively small depth below the surface of
 earth, the carbonates formed in the wet way also appear to
 go decomposition as a consequence of the rise of temperature,
 indicated by the streaming forth of carbonic acid at the places
 oned. Still these amounts of carbon, which are again put into
 lation, are probably much less than the amounts which, in the
 of carbonates, are withdrawn from circulation.

If we consider, now, that all organisms must have recourse to
 for the building up of their bodies, we see that the slow
 ation of the amount of floating carbon-capital which is taking
 on the surface of the earth must exercise a great influence on
 uilding of life. It can be regarded as highly probable that
 entially different state of affairs which, as may be concluded
 the investigations of the geologists, prevailed in former periods,
 due to the influence of the larger amounts of carbon dioxide
 present in the air, and that in the future also, organic life will
 go variation in such a sense that the continued diminution will
 t in a suitable manner.

Halogen Compounds of Silicon. —When a mixture of
 dioxide and charcoal is strongly heated in a current of dry
 ine, decomposition takes place, and there is obtained, besides
 monoxide, a volatile substance which analysis and vapour-density
 to have the composition $SiCl_4$. The reaction, therefore, takes
 in accordance with the equation $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$.
 ereas neither carbon nor chlorine alone can decompose silicon
 de, the decomposition can be effected when both substances act
 The reason of this is that by the simultaneous action

 the conditions existing in the tropics, a decomposition of the aluminium silicates
 place so that the silicic acid is removed and aluminium hydroxide remains

of the two substances, products are formed which are much more stable, or contain much less free energy, than when the substances act separately. For chlorine alone would yield free oxygen along with silicon chloride; charcoal alone, free silicon along with carbon monoxide; whereas, when they act together, the formation of substances with a large amount of energy, such as oxygen and silicon, is avoided. Of the principle which forms the basis of this reaction, use is frequently made.

Silicon chloride can also be obtained by the action of chlorine on amorphous silicon. It is a colourless liquid which boils at 59°, and has the density 1·5. In moist air it fumes strongly, since it is very readily decomposed by water to hydrogen chloride and silicic acid: $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$. This reaction shows it to be the chloride of silicic acid.

If silicon is heated not in a current of chlorine but in one of *hydrogen chloride*, the latter is decomposed and a chlorine compound of silicon, which also contains hydrogen and has the composition $SiHCl_3$, is formed. On account of the similarity of this formula to that of chloroform (p. 405), the substance has been called *silicochloroform*. It is a colourless liquid which looks like silicon chloride, and, like it, is also decomposed by water; it boils, however, somewhat lower, viz., at 36°.

Corresponding to these chlorine compounds, there are also bromine and iodine compounds which have an analogous composition, and which, in accordance with the general rule, have higher boiling points than the chlorine compounds, but which otherwise behave quite similarly, and are obtained in a similar manner. Silicon iodide is a solid at the ordinary temperature, and passes into a liquid only at 120°.

414. Silicon Hydride.— A compound of the composition SiH_4, is obtained, mixed with much hydrogen, when magnesium containing silicon is dissolved in hydrochloric acid. Since it can be liquefied much more easily than hydrogen, it can be obtained pure by cooling sufficiently strongly. It possesses the property of igniting spontaneously in the air, and owing to the formation of smoke rings of silicon dioxide, it gives rise to phenomena which are quite similar to those which are seen in the case of hydrogen phosphide. Its behaviour, also, with respect to the dependence of the spontaneous ignition on the density, appears to be similar to that of hydrogen phosphide.

Whereas, therefore, in respect of the formula, silicon hydride and methane (p. 404) are to be regarded as similar compounds, they exhibit very great differences in their chemical properties. Similar differences are also found in the case of many other compounds of carbon and silicon of analogous composition.

A hydrogen compound of silicon, Si_2H_6, analogous to ethane (p. 408), is also known. It is a colourless liquid which boils at -15° and freezes at -134°. It also takes fire spontaneously in the air.

117 Silicon Fluoride. With fluorine also, silicon combines, forming a compound of analogous composition, SiF_4, which at the ordinary temperature is a gas. This compound is very easily obtained by allowing hydrogen fluoride to act on silicon dioxide. Since it is decomposed by water, dehydrating agents must be added to destroy the action of the water which is formed in the process. This is most simply accomplished by treating a mixture of silicon dioxide and a saline fluorine compound (e.g. fluor-spar or calcium fluoride) with an excess of concentrated sulphuric acid. In place of silicon dioxide any silicate can be taken, since the hydrogen fluoride which is set free acts in the same way on all silicates.

This reaction is of great importance analytically, since it gives the means of bringing into solution, and thereby making accessible to analysis, the natural and artificial silicates, which otherwise show great resistance to chemical actions. For this purpose the silicates are heated with strong hydrofluoric acid and evaporated at a gentle heat. In this process a platinum dish must be used, as vessels of other material are attacked. The silicon fluoride passes off in proportion as it is formed, and the metals present are obtained as fluorides. Since these would give bother in the further analysis, the evaporation is completed with the addition of sulphuric acid, the fluorides thereby passing into sulphates.

Silicon fluoride is a gas at the ordinary temperature, and passes, under the influence of pressure and cold, into a liquid which boils at about -100.

In contact with water, silicon fluoride also undergoes change ; this, however, follows a somewhat different course from that in the case of the other halogen compounds. Instead of simply yielding hydrogen fluoride and silicic acid, an intermediate product, *hydrofluosilicic* ... is formed according to the equation $3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$.

Whereas the silicic acid separates out, the hydrofluosilicic acid dissolves in water and imparts to it an acid reaction. Where it is desired to obtain the latter, it is expedient to add so much hydrofluoric acid to the liquid that the silicic acid which separates out readily passes into solution again

$$Si(OH)_4 + 6HF = H_2SiF_6 + 4H_2O.$$
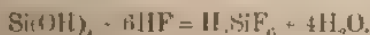
The yield of acid is thereby increased and the troublesome filtration avoided

Since the silicic acid which is formed would soon stop up the delivery tube, it is necessary either to use an inverted funnel, through which the gas is allowed to pass into the water, or the delivery tube is made to open under the surface of a layer of mercury placed at the bottom of the vessel of water (Fig. 107).

Hydrofluosilicic acid is known only in aqueous solution On

evaporating such a solution, the acid passes off entirely ; and if the
evaporation is carried out in a vessel of glass or of porcelain, an
etched spot is produced.   This is due to the fact that the hydrofluo-
silicic acid decomposes into silicon fluoride and hydrofluoric acid in
proportion as the solution loses water ; the former escapes as a gas, and
the hydrofluoric acid exerts its usual etching action.   While, therefore,
a solution of hydrofluosilicic acid does not itself attack glass, it does so
if it is evaporated.

* On these chemical processes depends the *etching of glass*, which
serves not only for the ornamentation of objects of daily use, but
still more important in the manufacture of scientific apparatus.   If a
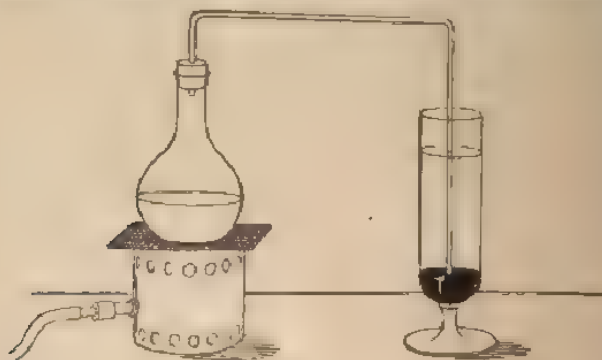glass surface is coated with wax, resin, or other substance capable of

Fig. 107

withstanding the action of hydrofluoric acid for some time, and this
coating is then removed where necessary, the surface of the glass, on sub-
sequent treatment with hydrofluoric acid, is attacked at all those parts
which are uncovered, while the protected parts retain their polish.

* For example, in order to graduate a burette (p. 189), a suitable
tube, on which the desired volume has been measured off, is coated
with melted wax and the necessary strokes made in this coating by
means of the dividing engine.   After marking the figures also, concen-
trated hydrofluoric acid is brushed into the marks and again washed
off after a few minutes.   If the wax is then removed, the marks are
found as hollowed lines in the glass, because the hydrofluoric acid
dissolves a part of the glass wherever it comes into contact with it.

* The etching can be performed more cheaply, but not so con-
veniently, by first preparing hydrofluoric acid from a mixture of
fluor-spar and sulphuric acid.   The object is then placed over the
mixture and the etching effected by means of the vapours of the acid
which are evolved.   This requires a considerably longer time, the
length of which depends on the tempe

* The etching produced by the vapours is *dull*, while that effected by the liquid acid is *clear*. This is due to the fact that in the first case only the gaseous silicon fluoride escapes, and the other constituents of the glass are left behind, while in the second case the glass is completely converted into soluble substances at the parts attacked. If to the aqueous acid substances are added which produce a precipitate on the glass, especially the alkali salts of hydrofluoric acid, a dull etching can also be obtained with the solution of the acid.

Hydrofluosilicic acid is a dibasic acid which forms many difficultly soluble salts. Thus the salts of the alkali metals, more especially, are most insoluble in water, and barium silicofluoride is so to such a degree that it is used for the separation of barium in analysis. The salt is stable in acid solution; by excess of alkali it is, however, decomposed with formation of a silicate and a fluoride. To this is due the peculiar behaviour in the titration of this acid with alkali, *e.g.* with caustic soda. If this base is added to a solution of hydrofluosilicic acid coloured with litmus, a blue coloration, certainly, is produced when an amount of the alkali has been added corresponding to the hydrogen of the acid. After a few minutes, however, this colour again passes into red, and twice as much soda can be still added before the solution remains permanently blue. This is due to the occurrence of the following reaction.—

$$H_2SiF_6 + 6NaOH = 6NaF + Si(OH)_4 + 2H_2O ;$$
$$or \qquad SiF_6'' + 4OH' = Si(OH)_4 + 6F'.$$
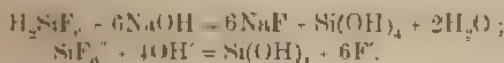
Sodium fluoride and silicic acid are formed. Since the latter does not act on litmus, the blue coloration occurs when 6NaF are formed.

On this behaviour of the salts of hydrofluosilicic acid an analytical method for the determination of the alkali metals can be based, since these form difficultly soluble silicofluorides, which experience the above decomposition.

446. Carborundum. Of the other compounds of silicon we shall still mention, on account of its technical importance, *silicon carbide* or *carbon silicide*. This is a greenish or black coloured mass obtained by allowing carbon to act on silicon dioxide at the very high temperature of the electric furnace $SiO_2 + 3C = SiC + 2CO$. The compound is distinguished by its very considerable hardness, and is therefore used in the arts as a grinding material. In chemical respects it is very resistant, since it is scarcely combustible, the silicon dioxide which is formed covering the surface with a coating which is impermeable for oxygen. It is slowly attacked when fused with caustic soda with access of air, sodium carbonate and silicate being formed.

Technically, the substance is called *carborundum*. Other mixtures prepared in a similar manner, but containing more carbon, are used for the manufacture of crucibles and for fire resisting stones.

2 F

CHAPTER XVIII

BORON

417 General.—Among the non-metallic elements, boron occupies a rather isolated position, since the elements most nearly related to it must be sought for among the metals, namely, among the earth metals. On account of the properties of the free element and of those of its compounds, it is, however, not expedient to give boron a place among the metals. It may best be classed along with silicon, from which it differs, however, in its typical compounds having a different composition.

Boron is a solid substance which is capable of existing in several different forms, one *amorphous* and at least one *crystalline*. Amorphous boron is obtained by passing the vapours of the chlorine compound over heated sodium, or, quite similarly to silicon, by igniting its oxygen compound with magnesium. After the removal of the admixtures, it forms a black powder of the density 2·5, which in many respects behaves similarly to charcoal, but is more easily oxidised; this occurs more especially by means of strongly oxidising solutions, even at the room temperature.

By the fusion of boron trioxide (*vide infra*) with aluminium, crystallised boron is obtained, which, on account of its hardness has been called "adamantine boron." It is not obtained quite pure in this way, but contains aluminium derived from its preparation. Since this metal is the element most nearly related to boron, the product is not to be looked upon as a compound, but as a mixture (possibly with a diamond-like form of aluminium isomorphous with boron, and not known by itself).

Boron containing carbon, and obtained from the two elements at a very high temperature, is of a similar character, and also possesses an adamantine hardness. This also ought most probably to be regarded as a solid solution, and not as a chemical compound.

The two forms probably stand to one another in the relation that amorphous boron is unstable with respect to the crystalline, as white phosphorus is with respect to red. In this case, however, the velocity

transformation at temperatures below a red heat is apparently immeasurably small.

The combining weight of boron is B = 11.

418. Boric Acid.—Of the compounds of boron, the most important are *boron trioxide*, B_2O_3, and the corresponding *boric acid*, which is formed from the trioxide by taking up the elements of water. The latter compound which, on analogy with orthophosphoric acid, may be called *orthoboric acid*, is represented by the formula $B(OH)_3$. Although it is known in the free state, salts of the acid are not known with certainty. On the contrary, all known salts are derived from "condensed" acids.

In nature, boric acid occurs as *sassoline* in lustrous, generally somewhat yellowish coloured scales, which have a soft and smooth feeling and are soluble in water. Hot water dissolves a large quantity, cold water comparatively little. The crude boric acid can, therefore, be easily purified by recrystallisation. The purification is still more successfully effected by converting the boric acid into its sodium salt, and decomposing this, after recrystallisation, in concentrated solution with an acid, e.g. hydrochloric acid. The boric acid then crystallises out as white scales.

Boric acid is a very weak acid, whose salts, on dissolution in water, are hydrolytically dissociated. The aqueous solution of the acid has a weak acid reaction, and conducts electricity only slightly better than pure water. Further, it cannot be titrated with caustic soda, since the alkaline reaction is gradually produced without a definite break between acid and base being observed.

On being heated, boric acid loses water and passes into boron trioxide. $2H_3BO_3 = B_2O_3 + 3H_2O$. The anhydride formed melts to a glass-like mass, which is viscous and can be drawn into long threads. The fused substance dissolves various oxides of metals, and can, therefore, be used in soldering; for this purpose, however, the more easily fusible alkali salts of boric acid are employed.

Boric acid has fairly strong antiseptic action, and is therefore used, as medicine and for pickling meat.

A very remarkable property of boric acid is that it is fairly readily volatile with steam, while its anhydride is highly resistant to heat. As a comparison with the other anhydrides, e.g. that of sulphuric acid shows, this behaviour is unusual, for in by far the greater number of cases the anhydrides are much more readily volatile than the acids.

On this volatility of boric acid with steam depends the method of obtaining it. In the volcanic districts of Tuscany, vapours containing boric acid issue from the earth. By first passing these vapours into water and evaporating this water at a lower temperature, crystallised boric acid is obtained. It has been found that boric acid is comparatively less volatile the more concentrated its solutions are; it is prob-

able also that its relative volatility diminishes with falling temperature. On this depends the fact that boric acid does not volatilise completely on evaporating its solutions.

With the vapour of alcohol, boric acid is still more readily volatile. In this case it is the formation of a compound, an ester (p. 407), which effects the volatilisation. If the alcohol is set on fire, the flame is coloured *green* by the volatile ester of boric acid. This phenomenon can be used for the detection of boric acid; if this is in the form of a salt, it is only necessary to rub it up with sulphuric acid and to pour alcohol over the mixture, in order to obtain the reaction.

As in the case of phosphoric and silicic acids, there exist also in the case of boric acid various "condensed" acids, which are derived from orthoboric acid, $B(OH)_3$, by the loss of the elements of water. From orthoboric acid only the monobasic "metaboric acid" can be directly formed in this way; much greater diversity, however, is produced when *several* combining weights of boric acid together lose the elements of water. Of the many such forms possible, we will mention only one, the dibasic *tetraboric acid* $H_2B_4O_7$, the formation of which is represented by the equation $4B(OH)_3 - 5H_2O = H_2B_4O_7$. This is the acid of the best known of all soluble borates, viz. borax $Na_2B_4O_7$.

The boric acids, like the silicic acids, form soluble salts with the alkali metals, whereas all other metals yield difficultly soluble salts. When heated, the borates fuse to glass-like masses; in this state they dissolve the oxides of the heavy metals, which then often exhibit characteristic colours. These phenomena serve for the detection of such metals in analysis. Borates are also added to glass and enamel, in order to impart to these particular properties, *e.g.* fusibility, small expansion with heat, and low power of refraction of light.

419. Other Compounds of Boron. — On heating amorphous boron, or a mixture of boron trioxide and charcoal, in a current of chlorine, there is obtained, as in the case of silicon, a readily volatile chlorine compound which condenses in the strongly cooled receiver to a liquid. In the pure state this is colourless, boils at 17°, and fumes strongly in moist air, since it undergoes decomposition with water to boric and hydrochloric acids: $BCl_3 + 3H_2O = H_3BO_3 + 3HCl$. From the vapour density, the molar weight of this compound is found to be 117, so that three combining weights of chlorine are contained in it. This is the reason why the combining weight of boron was not so chosen that its compounds could be formulated in accordance with those of silicon, which they resemble also in other respects. Similar reasons are furnished by the other halogen compounds of boron, which will presently be mentioned.

Boron trichloride can be regarded as the chloride of orthoboric acid, the three hydroxyls of which are replaced by chlorine. It may, therefore, be presumed that it is formed by the general method of

reparation of the acid chlorides, by the action of phosphorus penta-chloride on the acid. This is, as a matter of fact, the case, the reaction $(OH)_3 + 3PCl_5 = BCl_3 + 3POCl_3 + 3HCl$ being possible.

With *bromine*, boron forms a *tribromide*, which is quite similar to the chloride.

Boron trifluoride is obtained as a colourless gas, which fumes strongly in the air and is quite similar to silicon fluoride, by warming boron trioxide with fluor-spar and concentrated sulphuric acid. In water it dissolves with great rise of temperature and separation of boric acid; in the solution there remains hydrofluoboric acid, HBF_4. This, it is true, has a different composition from hydrofluosilicic acid, but behaves quite similarly; for example, it also forms difficultly soluble salts with the alkali metals.

The reaction takes place according to the equation $4BF_3 + 3H_2O = 3HBF_4 + BO_3H_3$.

Hydrofluoboric acid is also obtained by adding boric acid or boron trioxide to aqueous hydrofluoric acid; these are quickly dissolved with considerable rise of temperature.

Of the other compounds of boron, *boron nitride* should be mentioned. It is formed by the direct combination of boron with nitrogen, and is generally formed in the preparation of boron if air be not excluded. It can also be obtained by igniting boron trioxide with charcoal in a current of nitrogen. When pure, it forms a white powder which phosphoresces in the flame, and when heated to a moderate temperature with water vapour is decomposed to boric acid and ammonia: $BN + 3H_2O = BO_3H_3 + NH_3$.

CHAPTER XIX

ARGON, HELIUM, AND CONGENERS

420. Argon.—It has already been mentioned (p. 317) that the nitrogen obtained from the air differs from the "artificial," i.e. obtained from chemical compounds, in having a somewhat greater density. This at first puzzling phenomenon was finally explained (Rayleigh and Ramsay, 1894) by the fact that in atmospheric nitrogen another gas is contained which resembles nitrogen in its disinclination to form chemical compounds, and indeed, in this respect, is considerably its superior.

By converting the nitrogen of the air into non-gaseous compounds, the other constituent, which has been called *argon*, can be obtained pure. For this purpose there may be employed, for example, the property of nitrogen of combining with oxygen under the influence of the electric discharge (p. 327). The nitrogen peroxide thus formed is absorbed by caustic soda, and by adding the necessary amount of oxygen the reaction can be continued till all the nitrogen is used up. The excess of oxygen can then be easily removed by means of heated copper or phosphorus (p. 317). The same end is attained by the use of certain metals, e.g. magnesium or lithium, which readily absorb nitrogen at a red heat. A mixture of lime, magnesium, and some sodium has been found very suitable.

The residual gas is colourless, odourless, and tasteless, and has, in accordance with its density, the molar weight 40. It is, therefore, considerably more dense than nitrogen and oxygen. In the air it forms the 0·009 part by volume and the 0·012 part by weight, and the ratio of it to the other constituents of the air is not subject to any appreciable variations.

Since the gas does not form any compounds with other elements no combining weight, properly speaking, can be assigned to it. On the basis of the law of Gay Lussac (p. 142), it may, however, be assumed that if it did form any compounds, these must be formed with other gases in simple ratios by volume, and that, therefore, the normal weight 40, or some fraction of it, must be equal to the

combining weight. What this fraction is, however, cannot *a priori* be stated.

A decision can be here arrived at by means of the relation which has been found to exist in the case of other gases between the composition and the *capacity for heat*. By capacity for heat there is understood the ratio of the heat communicated to a body to the rise of temperature produced. This ratio is evidently all the greater, the greater the amount of substance subjected to the experiment. If it is referred to one mole (p. 159) of the substance, this special capacity for heat is called the *molecular heat* or *molar heat* of the particular substance.

If the amount of heat be measured in Joules (p. 121), and the ranges of temperature, as usual, in centigrade degrees, the following are the molecular heats of a number of gases :—

Oxygen gas	O	21	Carbon dioxid	CO₂	32
Nitrogen	N₂	20	Nitrous oxide	N₂O	30
Hydrogen	H₂	28	Water vapour	H₂O	28
Nitric oxide	NO	21	Phosphorous chloride	PCl₃	68
Carbon monoxide	CO	20	Chloroform	CHCl₃	69
Hydrogen chloride	HCl	20			

The smallest values of the molecular heats are, accordingly, 20, and are found in the case of those gases which contain two combining weights in the molar weight : it is thereby a matter of indifference whether the combined elements are like or different.

On determining the molecular heat of argon, however, the value 13 is obtained—a value, therefore, which is much smaller than that of all the gases given. This leads to the presumption that argon is still more simple in composition than these gases, *i.e.* that its molar and combining weights coincide, and that the formula of gaseous argon is given by the simple symbol A, and not A₂.

This presumption can be tested by analogy. From the chemical behaviour of *mercury*, the same conclusion has been drawn ; mercury vapour must also have the formula Hg and not Hg₂, since the combining weight and the molar weight have both been found equal to it. As a matter of fact, the determination of the molecular heat of mercury has yielded the value 13.

There is therefore sufficient reason for assuming the identity of molar and combining weights of argon, and for ascribing to this element the combining weight 40, whereby the formula of gaseous argon becomes A.

For the rest, argon behaves similarly to the other gases. At − 186°, at ordinary pressure, it becomes liquid. At − 188°, it solidifies.

If electric discharges are passed through rarefied argon, a spectrum of various lines is obtained. According to the pressure and the electrical conditions, three different spectra are obtained, the light in this case appearing blue, red, or white.

421. Helium, Neon, Krypton, and Xenon. A considerable time ago the name helium was given to an unknown element, the presence of which in the sun's atmosphere had been concluded from the occurrence of a strong and constant line in the yellow-green of its spectrum which could not be referred to any known terrestrial element. In his investigations on the occurrence of argon in minerals, the same line was found by Ramsay, one of the discoverers of argon, in the gases which are evolved on the ignition of certain minerals, e.g. cleveite, and he established the fact that it was due to a gas similar to argon, and it accordingly received the name helium.

Helium is found in some rare minerals which contain the element uranium, and is obtained from these by heating. From any nitrogen which may be present it can be freed in the same way as was given in the case of argon; from the argon which is sometimes also present, it must be separated by diffusion through a porous clay partition [1] (p. 94).

Helium is a very light gas, the molar weight of which is only 4; it is, therefore, only twice as heavy as hydrogen. Its critical temperature lies accordingly very low. For the rest it shares the properties of argon, and has, more especially, the small molecular heat 1·2, so that its combining weight must be put equal to its molar weight. With this value, He = 4, helium is, next to hydrogen the element with the smallest combining weight, so far as one can speak of such a thing in the case of an element which does not form any known compounds.

Further, in the residue from the evaporation of liquid atmospheric air, still a number of other gases have been discovered, which are characterised by their spectra and their density. They all likewise possess the small value of the molecular heat, and in all cases, therefore, the molar weight has been put equal to the combining weight. Their names are *neon* (Ne = 20), *krypton* (Kr = 81·8), and *xenon* (X = 128). Krypton boils at −151·7°, xenon at −109·1°. Their melting points are −109° and −140° respectively. Both of them are present in the air in exceedingly minute amounts; there being one part of krypton in seven million, and one part of xenon in forty million parts of air by weight.

[1] The separation is also effected by fractional distillation. On cooling the gaseous mixture of liquid air, the argon condenses and the helium remains as a gas, and so perhaps, is the liquid argon. On allowing the temperature to rise the helium escapes first. By repeating the liquefaction and gasification the gases may be separated. It

CHAPTER XX

General Remarks on the Chemistry of the Metals.—
Although the number of the metallic elements is much greater than that of the non-metals, the chemistry of them is much simpler and comparatively less diverse. This is due to the fact that by far the largest number and the most important of the compounds of the metals are saline in character. Now, we have seen generally, that the properties of the salts in aqueous solution are conditioned essentially by the properties of their ions. If, therefore, a metal, e.g. silver, forms only one kind of cation, the behaviour of all its salts in aqueous solution is known, if that of this particular cation is known; a knowledge of the anions, which have mostly been treated in the chemistry of the non-metals, is hereby supposed given.

So far, then, as the behaviour in aqueous solution is concerned, the chemistry of the metals is essentially given with the knowledge of the metal ions. In analytical chemistry we are concerned almost solely with aqueous solutions, and to what we there learn it is merely sufficient to add a statement of the solubility relations of certain difficultly soluble salts, in order to obtain the foundation of analytical chemistry. For general chemistry, however, it is necessary to add a knowledge of the compounds in the solid state as well as of the anomalous or indifferent compounds which also exist in the case of all metals, whereby greater diversity is produced.

Some variety is, however, found among the ions themselves. Most metals form not only elementary ions with different properties, the differences between which are connected with different valency, but they are also capable of forming with other elements *complex* ions with special properties. New groups of substances are thereby formed, and in this direction inorganic chemistry is developing a very great diversity, which at the present time is by no means exhausted—in many cases, indeed, its outlines are scarcely known.

In general, every anion will be able to form a salt with every cation. By virtue of a general rule, most of the salts in dilute aqueous

solution are extensively dissociated into their ions, so that *the prope* *of these solutions differ but little from the sum of the properties of the* Where, therefore, specific properties, which do not correspond to the rule, are met with in salt solutions, it can be concluded with certain that the dissociation of the salt present is *small*. From the com paratively great rarity of such exceptions, there follows, conversely the great generality of the rule just stated.

In the following descriptions of the different metals, therefore stress will be laid on the statement of the ions which can be formed from them, and the properties essential for their characterisation w be mentioned. In general, the methods employed for the detection and determination of the metals will be thereby given. To this there is added the chemistry of those solid compounds of the metals which are in any way important enough to find mention in this elementary work.

423. **Potassium.** While the knowledge of some of the potassium compounds can be followed back almost to the most remote move ments of culture, the characterisation of the potassium compounds as 'derivatives *of a special element* was first effected towards the end of the eighteenth century by Marggraf. On account of the preparation of potassium carbonate from cream of tartar, which is deposited in the barrels in the fermentation of wine, that compound received the name of *vegetable* alkali, in contradistinction to *mineral* alkali, soda carbonate or soda. Although potassium hydroxide or *caustic potash* could not be decomposed, it was long felt that it was no sim substance, but the actual proof that a *metallic* element formed the basis of the potassium compounds was first given in 1807 by H. D. who decomposed potassium hydroxide by an electric current deriv from a voltaic battery, which had just then been invented

After it had been obtained in this way, the method of preparing by purely chemical means was soon discovered, a method which w for long the only one employed. The most important of these reactions is the heating of potassium carbonate with charcoal; carbon monoxide and metallic potassium are formed, the latter of which volatilises and is condensed under rock oil : $K_2CO_3 + 2C = 2K + 3CO$ Quite recently the electrical method of preparing it has been aga adopted, since the necessary electrical energy can now be cheap generated in any desired amount.

Potassium is a silver white metal which melts at 62°, and which even at the room temperature, is so soft that it can be kneaded an easily cut with a knife. At 720° it volatilises; the vapour is lig green in colour. The colour can be rendered visible by heating the metal in a glass tube which is filled with a gas or vapour free from oxygen; the phenomenon, however, is visible only for a moment since the potassium vapour quickly attacks the glass, which thereby becomes covered with a black coating of liberated silicon.

... ... with very great readiness with oxygen, so
... ... almost all substances which contain that element
... ... under the joint action of the water vapour, it
... ... tarnished, owing to the formation of a layer of
... its metallic lustre can be observed only immediately
... has been made. If it is enclosed in a tube which
... dried with hydrogen, and then fused, the metallic
... be rendered visible and permanently preserved.

... of this property, potassium must be kept in such a way
... no access to it. In large quantities it is preserved in
... smaller quantities are kept under rock oil, since this
... not contain oxygen. It, however, absorbs gaseous oxygen
... potassium kept under rock oil soon becomes covered with
... crust which, however, only slowly becomes thicker and
... the metal fairly well.

... very remarkable that in *dry* oxygen potassium is not (i.e.
... very slowly) oxidised, whereas the smallest amount of water
... produces a rapid reaction. We have already (p. 101)
... examples of such catalytic acceleration of oxidation processes
... the presence of water. Such behaviour, however, in spite of
... generality, must not be regarded as universal, for instance
... processes have been proved (e.g. the combination of nitric
... with oxygen, p. 326) where the reaction takes place with un-
... velocity, even between the very carefully dried substances.
... concerning the determination of the combining weight of potassium
... all points have already been given under chlorine (p. 225)
... ... to K = 39·15.

Potassion.—Potassium can form only one kind of ion, viz.
... monovalent *potassion*, K'. With metallic potassium the formation
... place with very great ease and energy. The chemical properties
... of the metal are essentially characterised by this fact, for it reacts on
... substances in such a way that it passes into potassion, i.e. ...
... salt. Since, further, the passage of a *solid* salt into a *dissolved*
... is in general accompanied by only a slight change of energy, it is
... no essential importance for these reactions of potassium whether a
... dissolved or a solid salt is produced.

Isolated examples of such reactions have already been mentioned
the method of obtaining silicon and boron from their halogen com-
pounds may be recalled. Since in these reactions the halogen com-
pounds of potassium, i.e. salts of the metal, are formed, they ...
under the rule just stated.

The amount of heat which is liberated in the formation of pot. ...
from the metal is very great; it is found, in accordance ...
principles explained on p. 204, to be 259 kj.

If this quantity of heat is added to the heat of forma-
ation, the sum gives the heat of formation of the salt in ...

solution are extensively dissociated into
of these solutions differ but little from the
Where, therefore, specific properties, wl
rule, are met with in salt solutions, it
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by purely chemical means w
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volatilises and is condense
Quite recently the electric
adopted, since the necess
generated in any desired

Potassium is a silver-
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easily cut with a knife. Both kinds of solution are stable a
green in colour. The . . . limit, the supersaturated within
metal in a glass tube w . substances in all three physical states, and ca
oxygen: the phenome . . . be solid, liquid, and gaseous solutions of sol
since the potassium vac . . . however, the liquid solutions of solid subs
becomes covered with . . . that we shall, in the first instance, confine the dis

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. . . ms of a given substa
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. . . always the smallest, and t
. . . more soluble in proportion as t

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established. In the
bstance separates in

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polymorphic substance,
form of the same sub-
when both substances
te of equilibrium cannot
ited and the unstable be
then the unstable form has
stable form. This is the
which every solvent exercises

increased (e.g. by cooling down
ility increases with the tempera-
tate in which it does not deposit
at in which deposition occurs even
. The former state is called *meta-*
oundary between the two states is
their pronounced features are easily

another substance are added to a
mum changes, in general, only slightly,
saturated.
ppear to be great deviations from this
en mentioned (p. 232) that the solubility
ry small, but that large amounts of iodine
ontaining iodidion. At the same place this
that in the solutions produced the iodine
but was combined with iodidion to form the
turn, is partially dissociated into ordinary
iodine, I_2; and the latter is present in such
to the solubility in pure water.
imilar phenomena, therefore, which have the
se of the solubility, the conclusion may always
substance which has passed into solution has
e, whereby its actual has become smaller than its
ion.
cases of increased solubility, *diminutions* of the
so been observed. These are found especially in the
or quite definite conditions, and we shall now pass to
of these.
aviour of Salts.—Salts also behave, in the first instance,

Potassium cyanide is a white, very soluble salt, whose aqueous solution has an alkaline reaction and smells strongly of hydrogen cyanide. This is due to the fact that hydrocyanic acid is an extremely weak acid, whose salts are partially dissociated hydrolytically in aqueous solution; the carbonic acid of the air also has a decomposing action on the salt. Potassium cyanide is a powerful poison; in spite of this it is largely employed in the arts. It is used in photography to dissolve silver salts, also in electroplating with metals, especially in gilding and silvering, and finally, in very large amounts, for extracting the finely divided gold from the auriferous beds, especially in South Africa. Since all these applications depend on the formation of definite compounds with the heavy metals named, they can be explained in detail only under these metals.

In analytical and preparative chemistry, potassium cyanide is used as a powerful reducing agent, which allows of many metals being separated from their oxides and sulphides at its temperature of fusion. It is converted in the process into potassium cyanate and potassium thiocyanate respectively.

As to *potassium cyanate*, the essential points have already been given (p. 122). It is a white salt readily soluble in water, which on being acidified evolves carbon dioxide, while an ammonium salt is formed in the solution. This reaction, which depends on the transformation of cyanic acid, has also been already explained at the place cited.

Potassium thiocyanate, or sulphocyanide, $KSCN$, is the salt chiefly used in the applications of thiocyananion, SCN. It is a colourless salt which readily dissolves in water, at the same time producing a very considerable fall of temperature. It is easily obtained by heating potassium cyanide with sulphur.

450 **Potassium Oxalate.**—Oxalic acid forms with potassium not only the two salts which, according to the dibasic nature of the acid, are to be expected, but also another salt which can be regarded as a compound of oxalic acid with acid potassium oxalate. Of the salts of oxalic acid, those with potassium are the best known, because they occur in the juices of various plants, from which they were early prepared, and have led to the knowledge of oxalic acid.

Normal potassium oxalate, $K_2C_2O_4 + H_2O$, is a white salt soluble in water, and is used in photography.

Acid potassium oxalate, $KHC_2O_4 + \frac{1}{2}H_2O$, is called *salt of sorrel* because it was first obtained by evaporation and crystallisation from the juice of the wood-sorrel. It is less soluble than the normal salt, and is used for removing iron and ink stains, since it converts iron salts into soluble (complex) compounds.

Potassium tetroxalate is the name given to the salt $KHC_2O_4 + H_2C_2O_4 + 2H_2O$, which is easily obtained by mixing one of the previous salts with the necessary excess (or rather more) of oxalic acid in water.

hen the ions of the salts are regarded as independent con

us consider the simplest case, that of a salt consisting of two
ent ions, and let the concentration of the two ions be a and b,
the undissociated part c, then, according to the law of mass
... , the equation

$$a \cdot b = k \cdot c$$

d for every solution of the salt.
this equation k is the "equilibrium constant," which also
on the temperature.
the *saturated* solution, also, the same equation must hold. Let
esponding values be called a_0, b_0, c_0; the equation then

$$a_0 \cdot b_0 = k \cdot c_0$$

the right side of this equation are values which are constant at
temperature. In the case where a salt is simply dissolved in
two ions are produced in the same concentration,[1] and, there-
..., has a definite value. This value varies with the
and therefore the solubility of pure salts is in complete
with the general laws developed above.
ever, the two ions are present in different concentration, as
lutions of different salts are mixed, it is necessary for equili-
that the *product* of the two concentrations $a_0 b_0$ shall assume a
constant value. The greater the one concentration, therefore,
er must the other be in order that equilibrium be established.
luct $a_0 b_0$ which corresponds to equilibrium is, therefore, called
product In the case of difficultly soluble salts this is small;
soluble salts it is large. If the *product of the concentrations*
the ions present in a solution is greater than the solubility
of the corresponding salt, the solution is supersaturated in
of this salt, and so much of it must separate out that in the
solution the value of the solubility product is reached.
he product of concentrations in a solution is smaller than the
product of the corresponding salt, the solution exerts a
tion on the solid salt.
hese simple principles, the whole theory of precipitation and
on saline precipitates is contained. As simple also as it
diverse are its applications, and there will be frequent
ty in the sequel of making use of the light which is thrown
ormula.

consider ... the ... as well as states of equilibrium in ...
... from ... contri ... moles per
... wever, very small ... would merely ... , ... men
... employ the derived unit molecube.

quite small quantity of this mixture is added to the liquid to be test
for potassium and the whole well shaken, all possibility of supersat
tion is done away with, and a precipitate is therefore sure to be form
if the solubility product was exceeded.

Another precipitant which is greatly used for potassium, especial
in quantitative determinations, is *hydrochloroplatinic acid*, frequent
but erroneously called platinic chloride. It is a compound of th
composition H_2PtCl_6, and is, therefore, so far as the formula is co
cerned, similar to hydrofluosilicic acid, H_2SiF_6 (p. 431). A furth
similarity exists in the fact that both yield difficultly soluble salts w
potassium; whereas, however, hydrofluosilicic acid also yields a so
salt with sodium, and cannot, therefore, be used for the separation
the two elements; sodium platinochloride, in contrast with potassiu
platinochloride, is very readily soluble in water and alcohol.

If, therefore, hydrochloroplatinic acid is added to a solution co
taining potassium, the solubility product is exceeded even when th
concentration of the former is very small, and the salt K_2PtCl_6
generally called potassium platinochloride, separates out as a yel
precipitate, which microscopic examination shows to consist of regula
transparent octahedra. The reaction can be rendered much m
sensitive by the addition of alcohol, since the salt is much mor
difficultly soluble in alcohol than in water.

Since hydrochloroplatinic acid is a strongly dissociated acid of th
same order as hydrochloric acid, the presence or absence of hydr
is of no account, although it has an influence in the case of tartari
acid.

420. Potassium Hydroxide. When potassium is brought int
contact with water, violent action takes place; hydrogen is evolved
and usually takes fire in consequence of the high temperature produc
and the potassium is converted into potassium hydroxide $2H_2O + K$
$= 2KOH + H_2$.

The flame of the burning hydrogen has a reddish-violet colo
this is due to potassium, which imparts this colour to flames in whic
it is present. The potassium hydroxide which is formed does not, a
a rule, dissolve immediately in water, but forms a fused incandesc
ball which, on account of its high temperature, is not wetted by th
water; when all the potassium has been used up and the flame is e
tinguished, the ball still floats some time on the water until its temper
ture has so far sunk that wetting occurs. It then dissolves with s
great an evolution of heat that an explosive formation of steam occur
and small particles of the hot mass are projected in all direction
Since potassium hydroxide has a strongly corrosive action, the
particles can do considerable damage, and care must be taken by
timely covering of the vessel that they do not become scattered

The action of potassium on water is much more moderate whe
the metal is dissolved in mercury. This solution is called potassiu

..., amalgam being the general name for those metallic alloys
... contain mercury. In the laboratory it is prepared by dissolving
... potassium in mercury, considerable amounts of heat are set
... in the process.

On the large scale, potassium hydroxide is prepared by the action
... potassium amalgam on water, the necessary amalgam being prepared
... an electrical method. If a solution of potassium chloride is
... electrolysed, chlorine goes to the anode and potassium to the cathode.
The latter is formed of mercury, the potassium, after losing its
... electric charge, dissolves in it and forms potassium amalgam (p. 199)
... acts in another part of the apparatus on water, and is converted
... potassium hydroxide with evolution of hydrogen, in accordance
... the equation given above; the mercury, free from potassium,
... passes back to the cathodic space.

A solution of potassium hydroxide can also be obtained electro-
lytically by using an anode of some other metal, e.g. iron. In this
... no potassium at all separates out, but only hydrogen is evolved,
... the simultaneous formation of potassium hydroxide. It has
already been remarked (p. 198) that in this process we may look upon
potassium as being first formed, and then reacting secondarily with
water to give potassium hydroxide and hydrogen. Another, and per-
haps more correct view, is to regard the hydrogen as primary by
assuming that the hydrion, which is present in small amount in the
water is discharged and forms hydrogen. The corresponding amount
of ... remains in solution, and forms potassium hydroxide
with the potassium. In proportion as hydrion is thereby used up,
a fresh quantity is formed from the water. Both ways of viewing
the process lead practically to the same result, and the considerations
... cause the one or the other view to be regarded as the better
... not be put forward here, since at this point nothing of an essential
character depends on them.

* The method just given appears simpler than the previously
described mercury method. To it, however, there attaches the very
great difficulty that the cathodic space, in which the caustic potash is
formed must be very carefully separated from the anodic space, in
which the chlorine is evolved, since, otherwise, the two substances
would act on one another. At the same time it is required that the
electric current shall pass through unimpeded. The porous septa of
parchment paper, animal bladder, or clay which are usually employed,
... resist the simultaneous action of chlorine and caustic potash,
... use of the method is dependent on the satisfactory solution of
the "diaphragm question."

Further, potassium hydroxide is obtained by a chemical method
... decomposing potassium carbonate in dilute solution with calcium
... Since calcium is a divalent metal, the latter compound
has the formula $Ca(OH)_2$, and the reaction takes place in accordance

aqueous solution it is very extensively dissociated into its ions, and the properties of hydroxidion are, therefore, very strongly developed. Even in very dilute solution it colours litmus blue and phenolphthalein red. Somewhat stronger solutions have a soapy feeling because they dissolve the skin of the fingers and convert it into a slimy mass; they exhibit a similar solvent action on fats, horn, hair, and like animal substances. Acids of all kinds are neutralised, i.e. converted into potassium salts, and neutral salts containing other metals are mostly decomposed in such a way that potassium salts are formed and the metals are deposited as hydroxides.

Since the last reaction is largely made use of in analysis and for technical purposes, a short discussion of it will be given. If a solution
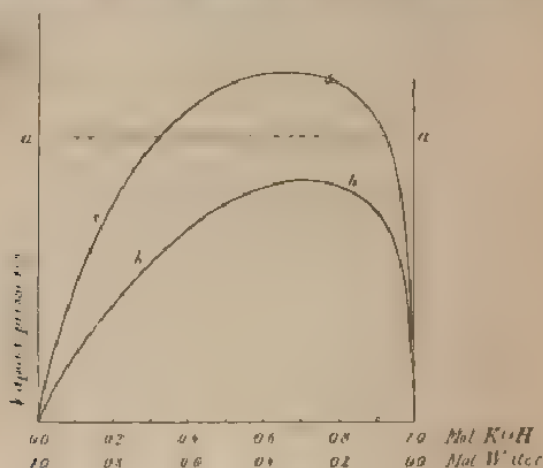
FIG. 108.

of caustic potash is added to the solution of a salt the metal of which forms a difficultly soluble hydroxide, this hydroxide will be precipitated, because so much hydroxidion is introduced into the solution by means of the potash that the solubility product of the hydroxide in question is greatly exceeded. Since, now, the hydroxides of almost all the metals except the alkali metals are less soluble than potassium hydroxide, their salts are all decomposed in the above manner by potash solution.

* Thus, solutions of zinc salts give a white precipitate of zinc hydroxide with caustic potash; solutions of nickel salts, a green, and of copper salts a blue precipitate of hydroxide. Ammonium salts on being heated after the addition of caustic potash, evolve ammonia gas, which can be detected by its smell and by the fumes which it gives with hydrochloric acid (p. 342), because the ammonium undergoes transformation with the hydroxyl to water and ammonia.

All these reactions are due to hydroxidion and not to potassion, for the same reactions are given when the latter is replaced by sodion or the ion of any other alkali metal. What has just been said is, therefore, not a description of caustic potash in particular, but of the strongly dissociated hydroxides in general.

The special properties of potassion have already been given (p. 443).

451. Potassium Chloride. The most widely distributed salt of potassium, and the one which is most important technically, is potassium chloride KCl. It occurs naturally in regular crystals as *sylvine*, and is found, however, in much larger quantities, united with magnesium chloride, as *carnallite*. The latter mineral will be described under magnesium, as will also the method of obtaining potassium chloride from it.

Potassium chloride is a colourless salt which is readily soluble in water, and which fuses only at a fairly high temperature (730°) to a colourless liquid which, on solidifying, forms the same regular crystals as are obtained from the aqueous solution. The solubility of potassium chloride in water increases almost proportionally with the temperature: at 0°, 100 parts of water dissolve 28 parts of the salt; at 100°, 57 parts (p. 218).

The solutions exhibit the reactions of the ions of the salt.

Being the cheapest potassium salt, potassium chloride is used for preparing numerous other potassium salts and as a *fertiliser*. Potassium is an essential constituent of plants; the quantity of this element required by the different plants is, however, different. More especially in the case of the sugar beet is a large amount of potassium necessary. Now, the normal soil contains rather considerable quantities of potassium, chiefly, it is true, in the form of compound silicates. On account of the slight tendency to decompose, these silicates are, however, available in such small amount that where there is a long continued occupation of the soil by plants which take up large quantities of potassium, a compensation by soluble potassium salts is necessary. This purpose is served by the manures containing potassium.

These are obtained from naturally occurring mineral beds which extend widely through North and Middle Germany; they have been worked with most success at Stassfurt. There, are found, lying on an enormous layer of common salt (sodium chloride), extensive beds of potash minerals (abraum salts), from the nature of which it is probable that we are here dealing with the residues of the evaporation of a former sea.

452. Potassium Bromide, KBr, is a white salt which crystallises in regular forms, is readily soluble in water, and is generally employed for all purposes for which bromidion is used. Large amounts of it are used in photography for the preparation of silver bromide; it is also used in medicine.

Metallic sodium is largely used in the arts and in the laboratory. Its former importance for obtaining other difficultly reducible metals has been lost, since the object can generally be attained more readily by means of magnesium or aluminium, or by the electrolytic method. It is used, however, as a powerful reducing agent in many reactions in organic chemistry, and for obtaining reactive intermediate products.

For these purposes, the metal is best employed in a condition in which it offers a large surface. Since, on account of the softness of the metal, it cannot be reduced to small pieces by blows or by filing, it is forced, by means of an iron screw press (Fig. 110), through certain openings, and is thus obtained in the form of wire or of ribbon, according to the shape of the opening. Since in this state the metal very rapidly oxidises in the air, the wire is allowed to fall directly into the liquid on which it is to act, or it is collected in a liquid which does not contain oxygen. Petroleum, which is usually employed for this purpose, has the disadvantage that it is difficult to remove; for chemical purposes, therefore, it is better to use readily volatile hydrocarbons obtained from the low boiling portions of petroleum (so called petroleum benzine or petroleum ether).
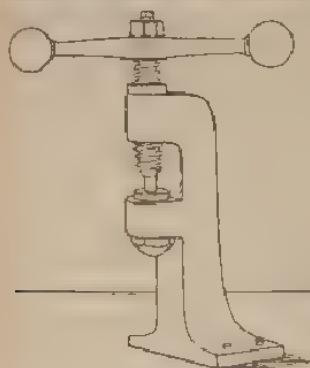
Fig. 110.

454. Sodion.—The description of the general characteristics which was given for potassion can be applied almost word for word to sodion. This also is a monovalent ion, which is colourless, and forms, almost exclusively, readily soluble salts. In this respect it is even superior to potassium, since there is scarcely a difficultly soluble salt of sodium known by means of which this ion could be readily and certainly detected. Further, there is no compound of sodium known which is formed in aqueous solution, by the colour of which it is possible to detect sodion. This is due to the fact that in all aqueous solutions which contain sodium, that element is present in the form of sodion, or, in other words, no sodium compound can be dissolved in water without being converted for the most part into sodion.

The *detection of sodium in analysis* would, therefore, be a matter of difficulty if it were not that there is another property by means of which it is rendered very easy. This is the yellow coloration which is imparted to a flame through the presence of sodium (p. 85). To what form or compound of sodium this yellow light has to be ascribed has not yet been determined with certainty, although it is very probably due to the incandescent vapour of elementary sodium; for the purpose

K and HF, along with the ions 2F' and H', as the dissociation
... ts of the ion HF.

Potassium Chlorate, $KClO_3$, is a salt which crystallises in
... drous monoclinic laminae, the solubility of which in water is
... at low temperatures, but very considerable at high. If the
... ty is represented as ordinates and the temperature as abscissa
... 75, p. 219) a curve is obtained which is convex on the under
... the increase of the solubility is not proportional to the
... rature, but is more rapid.

... formation of potassium chlorate by passing chlorine into a
... n of caustic potash, does not differ from that of sodium chlorate
... . Since in this process only a sixth of the potassium is con
... into chlorate, the potash is replaced by the cheaper calcium
... xide, which, in a perfectly similar manner, yields calcium chloride
... calcium chlorate. To the solution is added potassium chloride in
... at corresponding to the quantity of calcium chlorate; on cooling
... the liquid, the product of the concentrations of potassium and
... anion is considerably greater than the solubility product of
... um chlorate, and this salt, therefore, is deposited.

The chlorine required for the reaction is now no longer prepared
... chemical method, as formerly, but *electrolytically*. As was shown
... p. 451, hydrogen and caustic potash are formed at the cathode
... chlorine at the anode, when a solution of potassium chloride is
... lysed. While it is of essential importance to keep these two
... ets separate where it is a question of obtaining the caustic
... ash, they must be allowed to act on one another when the object
... prepare potassium chlorate, and, in contrast with the former
... it is especially advantageous to effect the mixing of the two
... stances as quickly and as completely as possible. In places, such
... Switzerland and Norway, where electrical energy can be obtained
... by means of water power, the whole amount of chlorates
... is now prepared in such a manner.

Since in this reaction all the potassium chloride can be finally
... verted into chlorate and only hydrogen is formed as by-product,
... chemical process can be summarised in the equation $KCl + 3H_2O$
$= KClO_3 + 3H_2$. Such a process does not take place spontaneously, since
... substances on the right side of the equation contain much more
energy (more both of total energy and of free energy) than those on
... it, from which they are formed. To make such a process possible,
... fore, free energy must be communicated, and this is done in the
... of the electric current.

The action of the latter consists in converting the ions which
... present into neutral substances (or, *vice versa*, neutral substances
... ions) at the electrodes. Since changes of energy always accompany
... transformation, two different cases may arise. In the first place,
... of the transformations may be accompanied by an *elimination*

Of exactly the same nature is a dark line in the yellow of the solar spectrum, which is obtained by regarding sunlight which has passed through a narrow slit, by means of a prism. Whereas, under these conditions, the light given by incandescent solid (or liquid) bodies yields a *continuous* spectrum, i.e. a coloured band in which the images of the slit, consisting of colours of all frequencies, follow each other without break from red to orange, yellow, green, blue, and violet, the light from the sun is discontinuous. In this case, certain colours, or light of certain frequencies, are missing from the coloured band, so that at these points dark images of the slit appear, which form dark lines across the spectrum parallel with the slit

Similar dark lines can be produced artificially by allowing the *continuous* light of an incandescent body to traverse a hot gas which of itself gives bright lines. These dark lines also appear at exactly the same points as the bright lines. Thus, a dark line in the yellow is obtained by bringing the flame of a spirit-lamp, on the wick of which some sodium salt has been strewn, before the incandescent fibre of an electric lamp, and regarding this through the sodium flame by means of a prism.

The cause of the production of these dark lines is found in the law (established by Kirchhoff in 1860) that substances which emit definite rays especially strongly, also absorb these same rays with especial completeness, the radiant energy being converted into heat or chemical work Or, to state it differently, emission and absorption depend in the same way on the oscillation frequency or the wave length.

In the experiment described above, the production of dark lines is due to the fact that of the continuous strong light of the incandescent carbon filament certain yellow rays are absorbed by the yellow alcohol flame and transformed into heat. At this point of the spectrum, therefore, only so much light is obtained as is emitted by the alcohol flame , and if this amount is less than the corresponding portion of the light from the carbon filament, the part appears *dark* in comparison with the surrounding portions To ensure the success of the experiment, therefore, the continuous spectrum must be very bright, but the absorbing gas mass only slightly luminous.

From these considerations, it is concluded that the sun consists of a highly luminous, and therefore very hot core, which yields a continuous spectrum. It is, therefore, probably liquid or solid. This core is surrounded by a gaseous mantle at a lower temperature and possessing feebler luminosity , in which the vapours of those substances are present the bright lines of which correspond to the dark lines of the solar spectrum. In this way the presence of more than half the elements found on the earth has been recognised in the atmosphere of the sun The chief elements present are hydrogen, sodium, calcium, magnesium, iron.

* 456. **Indirect Analysis.** If it is known that only the two

...assium chlorate which is almost exclusively used for this
...is due to the fact that it is, of all the chlorates, the one which
...longest known and is the easiest to prepare pure. In many
...wever, its slight solubility at medium temperatures is a dis-
...ge, it is then replaced by the much more readily soluble
...chlorate (which see).

...evolution of oxygen from fused potassium chlorate is greatly
...ed by the presence of foreign substances which do not take
... the reaction. In this respect, ferric oxide is the most
...; if finely powdered potassium chlorate is mixed with a fourth
...eight of ferric oxide and the mixture heated at one point, it
... incandescent, and decomposes with almost explosive violence.
...ar though feebler action is exerted by manganese dioxide,
... is therefore chiefly used to facilitate the decomposition of
...rate (p. 63).

... action is partly due to the fact that the fine powder of the
...es added facilitates the evolution of gas owing to the presence
...bubbles, as happens in the case of supersaturated gas solutions.
... decomposition of potassium chlorate into potassium chloride
...gen is not a process of dissociation which leads to a measurable
...d equilibrium, but a process which takes place only in one
...n, such as, e.g., the combustion of charcoal in oxygen. The
...n, also, practically cannot be reversed ; no measurable amount of
...um chlorate is formed by heating potassium chloride in oxygen.
...assium chlorate has, therefore, to be regarded as an unstable
...nd, whose existence depends on the fact that the decomposition
...it undergoes takes place so slowly as to be inappreciable by the
...ry means of detection. Even at the temperature of fusion, the
... of decomposition is not considerable when the substance is
...but is catalytically accelerated by the substances mentioned
... This follows from the fact that powders of approximately the
...gree of fineness and enclosing the same amount of air exert,
...same temperature, a very different action on the fused chlorate ;
... causes only a moderate, the other a violent decomposition.
...latter is all the more dangerous the larger the amount of salt
...posed at one time. From the thermochemical measurements it
...d that in the decomposition of potassium chlorate into potassium
...e and oxygen, 34 kj are evolved. From this it follows that
...it undergoing decomposition must rise in temperature ; the
...position is, however, thereby accelerated. If, by using com-
...ely large quantities, the dissipation of the heat is made small,
...perature rises so high that complete decomposition occurs in a
...hort time. These are, however, the phenomena of explosion.
...The catalytic action of the substances named can be demonstrated
...ily fusing pure potassium chlorate and waiting till the evolution
..., which usually occurs, has ceased. If into the quietly flowing

made in the determination of S, the error in the calculation of x will be greater. In the first example, it amounts to 4 per cent, in the second to more than 20 per cent, of which one can easily convince oneself by performing the calculation. This is due to the fact that the magnitude sought, x, is proportional not to the measured value S, but to the difference $S - k$, as the formula shows. If, for example, k is half as great as S, an error of one hundredth in S will be equal to an error of two hundredths in $S - k$, and, accordingly, the determination of x will be erroneous to the extent of two hundredths of its value. In general, the relative error in the result is to that in S as S is to $S - k$, and it becomes all the greater the smaller the difference $S - k$.

* The practical rules for the choice of indirect methods, which may be deduced from the above, will not be given here; on the contrary, it may be left to the student to think these out.

457. Sodium Hydroxide. The properties of this important compound have already been described, along with caustic potash; it forms the type of a strong base.

Towards water, caustic soda behaves in the same way as caustic potash; it dissolves with great evolution of heat to form a very concentrated solution, from which a hydrate $2NaOH. 7H_2O$ separates out in the cold. On evaporation by boiling, the solution passes, as in the case of caustic potash, into the fused, anhydrous compound. The reason of this behaviour, which differs from that which is usual in the case of solutions of solid substances, is the same as in the case of caustic potash. In moist air caustic soda takes up water and deliquesces, but it resolidifies again by absorption of carbonic acid much more quickly than deliquesced caustic potash, because the normal sodium carbonate is not deliquescent and is deposited in the solid state.

For the preparation of caustic soda, the methods given on p. 456 can be repeated almost word for word. It is now obtained by electrolysis from sodium chloride or common salt, whereas, formerly, it was almost exclusively obtained by the decomposition of sodium carbonate with lime.

If it is a question of obtaining small quantities of sodium hydroxide for laboratory purposes, we may start with *metallic* sodium and decompose this with water. One of the simplest methods of preparing it is to place metallic sodium (best in the form of wire or of ribbon) in a dish of platinum or of silver standing in a desiccator containing water. The sodium decomposes the water vapour and is converted into caustic soda, while the hydrogen escapes. The desiccator must, therefore, be furnished with a tube which allows the hydrogen to pass out without allowing the atmospheric carbonic acid to enter. For this purpose a tube filled with soda lime, i.e. a mixture of caustic soda and lime, is used.

It can also be prepared by pouring water over sodium amalgam,

...on crystallisation. This is another example of the fact that ...ic acids can yield acid salts like dibasic acids

...id potassium iodate is a substance which can be used in many ...volumetric analysis, since it crystallises anhydrous and can be ...weighed. On the one hand, by dissolving weighed quantities of ...tions of a definite *acid* titre are obtained ; it can, therefore, be ...the starting substance for the determination of acids and bases. ...ther hand, with excess of potassium iodide and acid, it gives ...ount of free iodine which can be calculated from the equation ... $= 10KI + 11HCl - 11KCl + 6H_2O + 6I_2$, so that it can also be ...the basis for iodometry (p. 300). However, it is not quite easy ...pare a salt of constant composition, for besides the salt just ...ned, there is a salt $KH_3I_2O_6$, which separates out from more ...ly acid solutions.

Potassium Carbonate, K_2CO_3, was, before the discovery of ...rman potash beds, the salt of potassium which was available in ...st abundance, and was therefore the most important. It is ...igated, because it was obtained from the ash of wood and other ...nt plants. In plants the potassium salts of organic acids occur ; ...the plants are burned, the carbon of the acids passes into carbon ...e and the potassium remains in the ash in the form of the ...ate

...obtain it from this, the ash is extracted with water ; the soluble ...of which the chief is potassium carbonate, are dissolved, and the ...er constituents remain behind. To obtain the salt itself, the ...on must be evaporated. The expenditure necessary for this is ...greater the greater the quantity of water, relative to the amount ...which has to be removed ; it is, therefore, of importance that ...tion should be prepared which is as concentrated as possible. On ...her hand, it is just as important to extract the salt as completely ...ble from the ash, for which purpose repeated extraction with ...water is necessary.

...e fulfilment of these two apparently opposed demands becomes ...ble by means of the principle of *counter currents*, already mentioned. ...there be given a series of vessels with ashes, A, B, C, . If, ...A is extracted with a certain quantity of water, the solution, on ...he hand, is by no means saturated with potassium carbonate, and, ...e other hand, a large amount of the salt remains behind with the ...since all the solution cannot be removed. For the extraction ...here is used, not pure water but the solution from A, and A is ...ted with a fresh portion of pure water. By this means a much ...concentrated solution is obtained from B and a much smaller ...ne remains in A. The solution from B goes to C and dissolves ...salt ; the solution from A is used for the extraction of the ...nes in B, and by a third quantity of pure water the salt still ...t in A can be almost completely removed.

aqueous solution of potassium carbonate has a fairly strong
action, and exhibits also the other characteristics of hydroxidion,
due to the fact that the ion CO_3'', which is the immediate pro-
dissociation of the salt, reacts with the water of the solution in
ce with the equation $CO_3'' + H_2O = HCO_3' + OH'$. Reactions
kind have been discussed at length in connection with phos-
nd (p. 367).

ssium carbonate is a convenient starting substance for the pre-
of other potassium salts. On the one hand, most free acids
corresponding salts with potassium carbonate, with evolution
dioxide. Carbonic acid is, as has already been shown (p 393),
weak acid, and this reaction therefore takes place with great
and completeness. On the other hand, carbonic acid forms
readily soluble salts with almost all metals except those of the
group. If, therefore, salts of those metals with any acids are
together with potassium carbonate, the solubility product of
responding metallic carbonate is exceeded, and the latter is
ated, while the potassium salt of the acid remains in solution,
hich it can be obtained by evaporation after filtering off the

Potassium Bicarbonate. – In the aqueous solutions of
um carbonate, the ion CO_3'' is, as has already been mentioned,
onverted by the action of the water into the ion HCO_3'; the
transformed, however, amounts to only a few per cent of the
antity. If, however, carbon dioxide be passed into the solution,
tion $CO_3'' + CO_2 + H_2O = 2HCO_3'$ takes place almost completely,
lution of the acid or primary potassium carbonate, $KHCO_3$, is
If the solution was concentrated, the solubility product of this
xcceded, and it is deposited in monoclinic crystals.

olution reacts fairly neutral, but still not so definitely as that
t of a strong acid, and dilute solutions exhibit even a distinctly
reaction. This is due to the fact that the first ion of the
carbonic acid, although much stronger than the second, is,
less, the ion of a very weak acid. Hydrolysis therefore occurs,
from the solvent water uniting with HCO_3' to form undissoci-
arbonic acid H_2CO_3, or its anhydride CO_2. The presence of the
mpound can be easily demonstrated by heating the solution;
fore the boiling point has been reached, bubbles of carbon
are evolved. In proportion as carbon dioxide escapes, more
acid. By reason, however, of the increasing concentration of
action, the equilibrium changes so as to become more and more
urable to carbon dioxide, and the evolution of the gas finally
practically to zero. The ratio of the concentrations at which
ccurs depends on the degree of dilution, more carbon dioxide
evolved the greater the dilution.

though, therefore, acid potassium carbonate is partially decom

the secretion of sodium is greatly promoted and a necessity for its replacement caused. In the case of animal food, however, the two elements are taken up in the proportions proper to the animal organism.

In the case of the vertebrate animals, the sodium compounds occur chiefly in the blood plasma and in the fluids of the body, while the potassium, as already mentioned, collects in the blood corpuscles.

From aqueous solutions of sodium chloride the well-known cubic crystals of the anhydrous salt separate out at temperatures above 4. Owing to the usually bad formation of these crystals, they enclose some mother liquor, so that when heated they give off small amounts of water. On being heated, the enclosed water is converted into vapour, the pressure of which increases as the temperature rises, until it becomes so great that the pieces of salt enclosing the liquid are shattered, whereby a crackling noise is produced. Having once undergone this treatment, the salt remains quiet on being again heated.

From concentrated solutions of sodium chloride at lower temperatures, a hydrated salt of the formula $NaCl + 2H_2O$ separates out in monoclinic crystals. These are stable only up to $+2$, if heated above this temperature, they melt and form a liquid from which the anhydrous salt immediately separates out in the form of small cubes.

* Even at the room temperature, these hydrated crystals are produced as an unstable form, when a solution of common salt is spread out in a thin layer on a glass plate and caused to evaporate rapidly by blowing on it. Under these circumstances, the separation of oblique crystals can be observed with a low power of the microscope; in a short time the ordinary cubes of common salt appear here and there, and these absorb the former crystals.

Common salt is used not only in food, but, being the most widely distributed salt of sodium, it is used as the starting point in the preparation of metallic sodium and of all other sodium compounds. Some of its transformations have already been mentioned; others will be discussed presently.

460. **Sodium Bromide** and **Sodium Iodide** are similar to sodium chloride, only more soluble than the latter. At lower temperatures both form hydrated crystals with $2H_2O$ of crystallisation, isomorphous with those of the hydrated sodium chloride. The temperature, however, at which they melt and pass into the anhydrous salts and the saturated solution of these, is higher. In the case of sodium bromide the conversion takes place at 50, in the case of sodium iodide at 67.

On investigating the solubility of these salts in water, and its change with the temperature, the relations are found which are represented in Fig. 111. The curve marked $NaBr + 2H_2O$ refers to the hydrated sodium bromide, that marked NaBr to the anhydrous salt. Similarly for the two forms of sodium iodide. As can be seen, each of the two forms has its own solubility curve, which is independent of

other. The point where the two curves cut is the point where the two forms can coexist along with the saturated solution. This is the temperature at which the hydrated crystals commence to melt. From this it follows that *each form of the salt has its own solubility*, and that the two forms have the same solubility at the temperature at which they change into one another. In this respect, therefore, salts with different amounts of water of crystallisation behave like the different forms of allotropic substances (p. 262).

As the diagram shows, the solubility curves are both produced
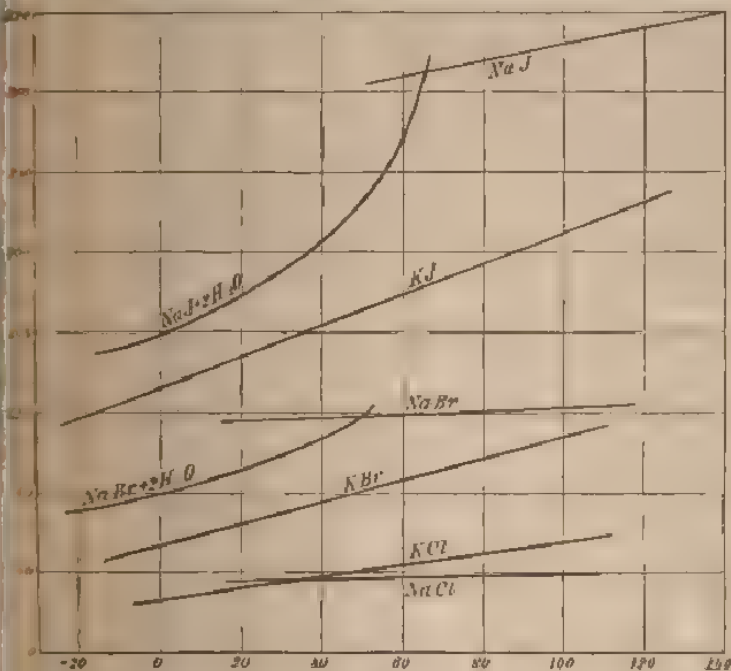
Fig. 111

beyond the point of intersection. This signifies that the transition does not *necessarily* occur here any more than in the case of the transition of allotropic forms, but that on both sides there may be supersaturation. An examination of the diagram also teaches that the less stable form has always a greater solubility than the more stable, so that a solution saturated in respect of the unstable form, on being brought into contact with "nuclei," i.e. already formed crystals, of the stable form, will deposit solid salt in this form; the solution is therefore, supersaturated with respect to this form.

If, for example, a saturated solution of anhydrous sodium bromide be made at 50°, and crystals of the hydrated salt are introduced into

it, the latter will grow and the residual solution will exhibit the smaller concentration which belongs to this form. On the other hand, a solution of the hydrated salt, saturated at 30°, will be found to be not saturated with respect to the anhydrous salt, i.e. it will be able to dissolve certain quantities of this salt. The presence of the hydrated salt must, however, be most carefully avoided, for excessively small quantities of this are sufficient to cause the separation of that form. If, however, the anhydrous salt is heated immediately before the experiment, all hydrated salt is destroyed, and the salt can be dissolved without fear.

The above discussion holds universally. It shows that *we can speak of the solubility of a salt or, generally, of a solid substance, only when we state the form which is in equilibrium with the solution*. In general, every form has its own solubility, and the point at which the solubility of the two forms becomes equal, is the transition point of the one form into the other.

Conversely, every curve representing the change of solubility with the temperature is, for each form, *continuous*. If a *break* in the solubility curve is observed, this is a certain proof *that the solid substance which is in equilibrium with the solution has passed into another form at the temperature of the break*.

461. Sodium Bromate.—The pure compound is of no special interest. Mixed with sodium bromide, in which condition the salt is obtained from bromine and caustic soda ($6NaOH + 3Br_2 = NaBrO_3 + 5NaBr + 3H_2O$), it constitutes a reagent which is used for liberating a known quantity of bromine in solution. On acidifying the mixture the same amount of bromine is set free as was used in the preparation of the mixture. The reaction can be expressed by the equation $HBrO_3 + 5HBr = 3H_2O + 3Br_2$, or, writing the ions, $BrO_3' + 5Br' + 6H^{\cdot} = 3H_2O + 3Br_2$. The mixture is obtained by adding bromine to caustic soda until the colour of the former is permanent, and then evaporating the solution; the excess of bromine is hereby driven off.

462. Sodium Chlorate.—In contradistinction to potassium chlorate, sodium chlorate is a salt which is very abundantly soluble in water. At the present time, therefore, when the method of preparing it on a manufacturing scale has become known, this salt is employed in many cases in which chloranion is used on account of its oxidising action, and where a more concentrated solution is desired than can be attained with potassium chlorate. It is obtained in a similar manner to potassium chlorate. It forms finely crystallised cubes and other forms of the regular system, and these have the property of rotating the plane of polarised light in a manner similar to quartz. Whereas, however, the latter exhibits this phenomenon in a regular manner only when the light passes through the crystal parallel to the chief axis, sodium chlorate rotates the plane of polarised light by equal amounts, no matter what the direction of the ray in the crystal is.

a consequence of the fact that these crystals belong to the
system, while those of quartz are hexagonal.

Sodium Nitrate.— This salt, which crystallises anhydrous
rhombohedra, melting at 320°, is, at the present day, the
important of the compounds of nitric acid. It is found in large
in Chili. Since no rain falls in those districts, it has been
for this salt to be preserved. How it has been formed
yet, not be stated with certainty or probability ; the constant
in it of iodine compounds in the form of sodium iodate,
in favour of its formation from the salts of sea-water. It is,
still a mystery what conditions existed to produce such a
oxidising effect that, along with the nitrate, the iodine
have passed into the iodate, and even a portion of the chlorine
chlorate (which is also found in Chili saltpetre under certain
to the extent of several per cent). We may, perhaps,
that at the time of the formation of this salt some cause was
by which unusually large amounts of ozone were produced ; the
of this would render the formation of these highly oxidised
from any sodium compounds present, intelligible.

crude sodium nitrate is mixed with earth and clay, and is
by a simple process of crystallisation. The purification can
and successfully carried out by this method, since the solu-
of this salt changes very greatly with the temperature, as can
from the following table :—

SOLUBILITY OF SODIUM NITRATE

Temperature.	100 gm. water dissolves
0	68·8 gm. of NaNO₃
10	72·9 ,,
20	87·5 ,,
40	102 ,,
60	122 ,,
80	148 ,,
100	180 ,,
110	200 ,,

sodium nitrate is used in large quantities for manuring purposes ;
the most important artificial nitrogen manure for cultivated
and its application is limited only by the price. The nitrogen
easily available for the plant in the form of nitramin, and
manure has, therefore, the quickest action. Since, however, the
not retain this substance, as it does potash, phosphoric acid,
the manuring with Chili saltpetre must be carried out
diately before the time when the plant requires the nitrogen
sodium nitrate is further used in large quantities for the prepara-
of nitric acid (p. 321), and for conversion into potassium nitrate
It is also used in the preparation of nitro-compounds ; for
purpose, the nitric acid is not first prepared from the salt, but a

mixture of sodium nitrate and sulphuric acid, which on distillation would give nitric acid, is directly employed. Lastly, a considerable portion of the salt is converted into sodium nitrite, which is employed in enormous quantities in the preparation of artificial dyes.

Sodium nitrate cannot be used in place of potassium nitrate for the preparation of gunpowder and blasting powder, because the powders made from it become moist.

Since the Chili saltpetre deposits are approaching exhaustion (in some decades), the production of nitrates or of free nitric acid from other sources is beginning to be a matter of importance.

464. **Sodium Nitrite**. —At the present day, sodium nitrite is manufactured and used in large quantities in place of potassium nitrite, from which it differs in the ease with which it can be prepared pure. It is a very soluble salt with a feebly alkaline reaction; when treated with acids, it evolves red fumes of the oxides of nitrogen (p. 332). It is obtained, similarly to potassium nitrite (p. 472), by heating sodium nitrate with metallic lead.

465. **Sodium Sulphate**. —The normal sodium sulphate, Na_2SO_4, is well known in the form of hydrated crystals of the composition $Na_2SO_4, 10H_2O$, by the name of *Glauber's salt*. It received its name from Glauber (born about the year 1640), a physician and chemist, who introduced it as a drug; he ascribed to it great healing power, and gave it the name "sal mirabile." Its action on the human organism consists essentially in the fact, that when it gets into the intestines, it makes their contents more watery and thereby facilitates the evacuation.

* This action arises from the fact that the walls of the intestines offer considerable hindrance to the diffusion of Glauber's salt. The *equalisation of concentrations*, the tendency towards which is exerted under all circumstances, cannot, in this case, be accomplished by the dissolved substance mixing with the body fluids, but, on the contrary, water must pass from the latter into the intestine.

* From this it follows that all other salts which have the same property of not passing through the intestinal walls, and which do not exert any other actions on the organism, must also behave in the same way. This is, indeed, the case; magnesium sulphate (Epsom salt) acts in exactly the same way as Glauber's salt.

The solubility relations of sodium sulphate are rather complicated, and are represented in Fig. 112. Three different solubility curves can be distinguished, belonging to three different forms of the salt. Of these forms, one, stable at higher temperatures, is anhydrous; at medium temperatures, ordinary Glauber's salt with $10H_2O$ of crystallisation, is stable; besides these, an unstable salt can be obtained at lower temperatures containing $7H_2O$ of crystallisation.

On following the curves in Fig. 112 from right to left, we have, in the first place, the curve of the anhydrous salt, marked a, which, in

contrast with the behaviour of most salts, ascends as it passes in the direction of lower temperatures. The fact that the solubility of the salt *diminishes with rising temperature*, is connected with the other fact

that the salt dissolves in
its almost saturated solu
tion, with *evolution* of
heat, or, absorption of
heat occurs when it sepa
rates out from a super
saturated solution (p.

Fig. 112

The curve of the
anhydrous salt can be
followed downwards to
about 20°. From 32°
upwards, however, the
solutions are *supersatur*
ated with respect of the ordinary Glauber's salt with 10H$_2$O, and
they can therefore be obtained only when the presence of this latter
salt is strictly avoided. This requires some care, for, as we shall see
presently, the salt is everywhere present in dust.

At 32°, the curve of the anhydrous salt is cut by the solubility
curve of *Glauber's salt* (marked with 10); at this point, therefore,
both salts can exist along with the solution, since at this point the
saturated solutions contain the same amount of salt. This state is
most easily obtained by heating Glauber's salt to 32°. It appears
then to undergo fusion. We are here dealing, however, with a more
complicated process, for the liquid does not have the same composition
as the solid Glauber's salt, but contains more water. This is due to
the fact that *anhydrous* salt separates out at the same time; for this
reason, the salt does not pass into a clear liquid, no matter how long
it is heated, but forms, after the Glauber's salt has disappeared, a
mass of anhydrous salt and saturated solution.

The transition temperature of Glauber's salt is, when a pure
specimen is employed, exceedingly constant, so that it can be used,
like the melting point of ice, for readily obtaining an unvarying
temperature. The temperature is 32·383 on the international hydro-
gen thermometer scale.

The solubility curve of Glauber's salt with 10H$_2$O, can be followed
downwards to somewhat below 0°. The solubility of the salt di
minishes very rapidly as the temperature falls, so that at 0° the liquid
contains only 0·05 of sodium sulphate (calculated as anhydrous salt).

So far as we have yet considered the relations, we are dealing
with two independent solubility curves, of which the one belongs to
the anhydrous salt, the other to the salt with 10H$_2$O. The present
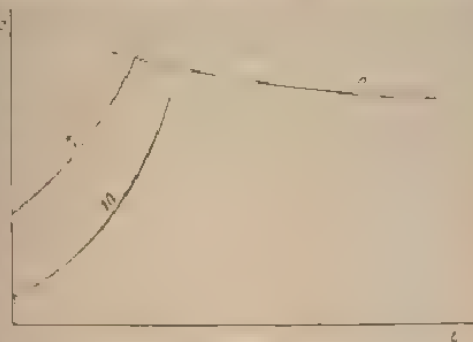case is distinguished from that of sodium bromide and sodium iodide

only by the fact that one of the curves slopes downwards, while in the case of the latter salts, both curves slope upwards.

It has to be specially noted that the break in the solubility curve at 32 is due solely to the fact that the *solid phase* in the solution equilibrium changes at this temperature. It was formerly thought that something special took place in the solution at this temperature, such as, say, that below 32 the salt was dissolved in a hydrated form above that temperature, in an anhydrous form; even now, such unfounded views are sometimes met with. However, on investigating the properties of the *solution* at its passage through this point, no sign of break was found, and so far as the solution is concerned, this temperature is in no way distinguished from other temperatures. The only thing that changes at this temperature is the nature of the *solid* salt, and this is the all sufficient reason for the occurrence of the new solubility curve.

The phenomena, now, become somewhat more complicated from the fact that solutions can be fairly easily prepared which are considerably supersaturated with respect to the salt with $10H_2O$. Indeed the phenomenon of supersaturation has in no case been studied more fully than in the case of Glauber's salt.

Such supersaturated solutions are obtained by heating Glauber's salt with half its weight of water until all solid particles have disappeared, closing the vessel and allowing it to cool down. The stopper does not require to be *air* tight but only *dust* tight; a plug of cotton wool, for example, is therefore sufficient. If this is removed, after the solution has cooled down, crystallisation, as a rule, commences at once. This is due to the fact that Glauber's salt is extremely widely distributed in the dust of towns, being formed from the compounds of sodium everywhere present (p. 479), and the sulphurous acid which is produced in the combustion of coal, and is derived from the sulphur therein contained. If the experiment is carried out in the country far from such sources of dust containing Glauber's salt, the crystallisation can also be excluded. Since it was for long not believed that this was the cause of the "spontaneous" crystallisation of Glauber's salt, the crystallisation of the supersaturated solution appeared as something peculiar and mysterious. By working with other substances, however, which do not, or only rarely, occur in the dust, one can convince oneself that in general supersaturated solutions possess a great stability, and that it is only towards nuclei of their *own* solid substance that they are unstable.

* The amounts of solid substance which give rise to crystallisation are small but not immeasurably so. The limit lies about one millionth of a milligram.

On cooling down a supersaturated solution of Glauber's salt to about 5, other crystals make their appearance, which have the composition $Na_2SO_4 \cdot 7H_2O$, and whose solubility curve is also given in

§ 112. Throughout its whole course, this curve lies above the curve of the salt with $10H_2O$, from which it follows that the solutions saturated with the salt 7, are always supersaturated with respect to salt 10. If, therefore, some of the salt 10 is introduced into a system composed of salt 7 along with solution, the solution will, in the first place, deposit salt until the point of saturation with respect of 10 is reached, i.e. the concentration of the solution will reach that point on the curve 10 which lies below the former point on curve 7. This solution, however, is unsaturated with respect to 7; consequently, this salt must dissolve. The solution thereby again becomes supersaturated with respect to 10, and this separates out. This evidently goes on until, finally, all the salt 7 has disappeared and is replaced by 10.

It may be asked, Why does the unstable salt 7 separate out first at 15°, since, of course, the solution could give the stable salt 10 directly? The answer is to be found in the universal rule that the *less stable must first appear* (p. 210).

Finally, if the solution be cooled down to about −15°, Glauber's salt separates out spontaneously from it and supersaturation ceases, and this too without a nucleus of the solid salt being necessary. The region, in which the separation does not occur without such a nucleus, can be distinguished as the *metastable region*, from that region, the *labile region*, in which separation takes place without a nucleus. Increase of supersaturation leads, in the first place, into the metastable region, and from this then into the unstable. The limits of the two regions are, however, difficult to fix, since the presence of dust has a great influence on the spontaneous formation of solid forms from unstable liquids.

The crystals of Glauber's salt *effloresce* in the air, i.e. they lose water and become converted into a fine white powder of anhydrous salt. The cause of this is that the vapour pressure of Glauber's salt (or more exactly, of a mixture of Glauber's salt and anhydrous salt) is greater than the mean vapour pressure of the water in the air (p. 126), so that the salt must lose water and pass into anhydrous salt.

On the basis of this remark, the objection may be made to the explanation of the crystallisation of supersaturated solutions of Glauber's salt by dust, that according to the above statement there can be no Glauber's salt present in the dust, but only *effloresced* Glauber's salt, i.e. *anhydrous* salt. This is so; nevertheless, experiment shows that even effloresced Glauber's salt can also effect the crystallisation of the supersaturated solutions, and loses this property only when it has been heated. In the effloresced salt at the ordinary temperature, then, there are apparently sufficient traces of unchanged Glauber's salt present to bring about crystallisation. Or, there is produced on efflorescence, a form of the salt which in contact with the solution immediately gives Glauber's salt, a behaviour which the

anhydrous salt certainly does not show, after it has been heated. Which of these two possibilities corresponds to the truth, has not been determined.

Intact crystals of Glauber's salt can be kept in dry air without efflorescing; if, however, efflorescence has once begun at any point, it spreads out from that point, and this it does in accordance with a law which is determined by the crystalline form of the efflorescence salt (p. 264). We have here again a phenomenon of the nature of super saturation, which can be removed only by the presence of a further phase. Applying the phase law to this case, we obtain the following:— Since the given system consists of two components, sodium sulphate and water, the sum of phases and degrees of freedom is 4. If hydrated salt and water vapour are given as two phases, the system has still two degrees of freedom, i.e. at a given temperature, every value of the vapour pressure (within certain limits) can exist. It, however, another phase is added, only one degree of freedom remains, i.e. to every temperature there belongs a definite pressure. Such a system, therefore, behaves as a pure liquid, for it has a definite vapour pressure which is independent of the amounts of the phases, i.e. independent of the relative quantities of Glauber's salt, anhydrous salt, and water vapour. Observation shows that such a law does indeed hold, only this pressure is established more slowly than in the case of a liquid.

Since both solid phases are required for the definition of the system just considered, it follows that one cannot speak simply of the vapour pressure of a hydrate: on the contrary, it must be stated what other solid (or liquid) substance is also in equilibrium with the vapour. Many salts form several hydrates: every combination, therefore, of two hydrates (or of a hydrate and the anhydride) must have its own vapour pressure. This also has been confirmed by experiment.

Besides being used for medicinal purposes, sodium sulphate is also employed as such in the manufacture of glass and in some other industries. It occurs as a by-product, and as an intermediate product in much larger quantities. As a by-product, it is obtained in the preparation of hydrochloric acid from common salt, and of nitric acid from sodium nitrate. The greater part of the salt is converted into sodium carbonate or soda. The methods by which this is accomplished will be discussed immediately.

Sodium sulphate also occurs in nature. As a mineral, it is called thenardite. It is a very frequent constituent of the natural waters; waters which contain large quantities of this salt in solution, such as the Carlsbad waters, are used as mineral waters for the removal of disturbances of the nutrition.

466. Acid Sodium Sulphate. The salt NaHSO$_4$, is prepared in the same manner as the corresponding potassium salt, is used for the same purposes, and exhibits the same chemical relations.

467. Sodium Sulphite.—The normal salt of the composition

O . 7H₂O, occurs in commerce in large crystals ; it is chiefly used
photography for adding to the "developers" to preserve these
against the oxygen of the air. The developers are alkaline solutions
contain organic compounds, the purpose of which is to reduce the
compounds of the exposed photographic plate to metallic silver.
The sulphite, it is true, scarcely possesses the power to effect this
action, but it prevents to a certain degree the oxidation of the
developer in the air, and so keeps this for a longer time uncoloured and
fit to be used.

The salt dissolves readily in water. On being heated, it decom-
poses, similarly to sodium sulphate, into anhydrous salt and a saturated
solution; its solubility exhibits corresponding changes.

When exposed to the air, the crystals soon become covered with a
coating of powdery sodium sulphate, which is formed by the oxidation
of the salt. It can be seen, therefore, from the appearance of the salt,
whether it is still fit to be used or not.

Acid sodium sulphite, NaHSO₃, is also known. It is deliquescent,
and oxidises in the air still more readily than the normal salt. Its
concentrated solution is used in the arts.

Sodium Sulphide.—With regard to the behaviour of the
aqueous solutions of sodium sulphide, Na₂S, and of sodium hydrosulphide,
NaHS, the reader may be referred to what was stated in the case of
potassium sulphide (p. 466). With regard, however, to the *solid salts*,
it may be mentioned that from solutions of sodium sulphide, well
formed crystals belonging to the quadratic system, and containing
9H₂O of crystallisation, can be obtained. Anhydrous sodium sulphide
is obtained as a flesh-coloured mass by the reduction of sodium
sulphate with charcoal

Impure mixtures of various polysulphides of sodium, along with
sodium sulphate or sodium thiosulphate (according to the temperature
employed) which are prepared under the name of *liver of sulphur* by
fusing together soda and sulphur, are used in medicine and in various
industries

Sodium Thiosulphate is the best known salt of thio-
sulphuric acid (p. 298). It is obtained by warming solutions of normal
sodium sulphite with sulphur; the latter is dissolved, and the solution
then contains the salt Na₂S₂O₃, the composition of which differs from
that of the sulphate only by one combining weight of sulphur. From
the solution it is obtained by evaporation in the form of large, trans-
parent crystals of the monoclinic system containing 5H₂O of crystal-
lisation

In the manufactures, sodium thiosulphate is prepared from the
calcium sulphide of the "soda waste" (p. 499); by oxidation in the air,
this is converted into calcium thiosulphate, which is then transformed
into the sodium salt by means of sodium sulphate.

The salt is used in large quantities. To a certain extent it is

used in photography for "fixing." It has the property of dissolv
difficultly soluble salts of silver, and pictures which have been pr
from these are treated with this salt in order to remove the unchar
silver salt, and to render the pictures unchangeable by light.
theory of these processes will be given under silver.

Further, thiosulphate is used in large quantities as an "antichlor"
for the purpose of removing the last traces of free chlorine from the
fibres of material which has been bleached by its means.   Free chlorine
is converted by this salt into chloridion, which is harmless; at the
same time, sulphuric acid is formed.   The reaction can be written
$Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2NaCl + 2H_2SO_4 + 6HCl$, or $S_2O_3'' + 4Cl_2$
$5H_2O = 2SO_4'' + 8Cl' + 10H.$

Bromine acts similarly to chlorine.   Iodine, on the other hand,
converts the thiosulphate only into tetrathionate.   Since the reaction
has already been discussed on a former occasion (pp. 299 and 300)
shall only repeat the equation here : $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2Na$
or, writing the ions, $2S_2O_3'' + I_2 = S_4O_6'' + 2I'.$

Sodium thiosulphate is used, therefore, in volumetric analysis for
the determination of free iodine.   For this purpose, it possesses the
very important advantage that its solutions keep perfectly in the air
and are not oxidised.   In this respect it is greatly superior to sodium
sulphite, which was formerly used for the same purpose.   Care, only
must be taken that the solution of thiosulphate does not become acid,
in very dilute solutions, even the carbonic acid of the air effects the
decomposition described on p. 298, with deposition of sulphur.   Since
the iodine reaction is very sensitive, it is just here that one preferably
uses dilute solutions ; these must, therefore, be prepared shortly before
being used.   This is best done by diluting a measured amount of a
concentrated stock solution (e.g. a normal solution) which remains un-
changed for a long time.   Such a normal solution contains, in accord-
ance with the above reaction equation, one mole or 248·34 gm. of the
crystallised salt $Na_2S_2O_3 + 5H_2O$ in a litre.

If a solution of sodium thiosulphate is added to a solution contain-
ing iodine, which may be neutral or acid, a corresponding amount of
the free iodine disappears ; the complete disappearance can be readily
recognised by adding some dissolved starch and titrating till the blue
colour of the starch iodide disappears.

This volumetric method is not limited to the determination of free
iodine, but can, evidently, be applied to all substances which either
form iodidion from iodine or, conversely, convert iodidion into free
iodine.   To the latter belong most of the oxidising agents ; to the
former, many reducing agents.   Thus, free chlorine or bromine as well
as chloric acid, hypochlorous acid, iodic acid, etc., can be titrated by
adding to them an excess of potassium iodide and determining the
amount of iodine liberated by means of thiosulphate.   As an example
we shall describe the determination of potassium iodate.   In ac

equation, this reacts with potassium iodide according to the equation $KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$, or, written in ionic form, $IO_3 + 5I + 6H = 3H_2O + 3I_2$. For every mole of iodamon, six combining weights of free iodine are formed, and, therefore, six moles of sodium thiosulphate are used.

Reducing substances can be determined by bringing them together with a measured excess of free iodine (dissolved in potassium iodide), and titrating the amount of iodine remaining after the reaction, with thiosulphate.

For some reactions it is of importance to notice that in the interaction of iodine and thiosulphate, the alkali titre of the solution does not change. In other words, hydrion is neither used up nor formed in this reaction.

If the crystallised salt is heated to 56°, it melts without leaving a solid residue; it behaves, therefore, differently from sodium sulphate or sodium sulphate. The fused salt may be allowed to cool without crystallising; if, however, a particle of the solid salt is introduced, crystallisation commences at once. This fused substance is especially fitted for showing that crystallisation is effected only by the presence of the solid salt, and does not consist, say, in a disturbance of "the unstable equilibrium of the atoms." Thus, if a glass rod whose end is covered with a firmly adhering coating of the salt (all loose particles must be carefully removed) is introduced into a fairly large amount of the cooled fused thiosulphate, crystallisation proceeds solely from the end outwards, and after a few seconds the glass rod with the bunch of crystals adhering to it can be removed from the liquid, *without this ceasing to crystallise.*

470. Sodium Carbonate. Normal sodium carbonate, Na_2CO_3, is a white salt which readily dissolves in water with alkaline reaction; when anhydrous it melts at 850°, and can unite with water to form various hydrated compounds.

Besides the anhydrous salt, at least four hydrates are known with certainty. By boiling down a hot saturated solution, a salt of the formula $Na_2CO_3 + H_2O$ is deposited. If the solution is allowed to cool down in the air, the ordinary crystallised salt containing $10H_2O$ is obtained. On cooling down the hot saturated solution, with exclusion of heat, two different salts are obtained, both of which contain $7H_2O$, but have a different crystalline form and also a different solubility. Which of the two is formed, depends essentially on the concentration of the solution.

Besides these salts, other hydrates with 3, 5, and 15 molecules of water of crystallisation have been described.

Each of these hydrates has its own solubility, and the different solubility curves cut one another in a manner similar to that described in the case of Glauber's salt. The most stable forms are those with $10H_2O$ and with $1H_2O$; these two behave to one another essentially

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sulphur from them in some form or other, and at the present day this is successfully carried out in those works where the Le Blanc process is still in use. Since, however, the disappearance of this process is only a question of time, it is not necessary for us to enter into a description of the methods of "sulphur regeneration."

The new method, which on the Continent has practically entirely replaced the older method, depends on the following reactions. Ammonia is absorbed by a solution of common salt, and carbon dioxide then passed in. Sodium bicarbonate, which separates out in the solid state, and ammonium chloride, which remains in solution, are formed. The latter is decomposed with lime into calcium chloride and ammonia, and the ammonia formed is used again in the preparation.

The chemical process, then, amounts to this, that the ions Na', NH_4·, Cl', and HCO_3 are brought together in concentrated solution. Under these conditions, there will be deposited, in accordance with principles already laid down (p. 446), that salt which has the smallest solubility; in this case, sodium bicarbonate. It is true that neither ammonia nor carbonic acid alone is dissociated to any great extent into ions, but the two immediately form ions when they come together in solution, since the ammonium bicarbonate is a salt which in solution is dissociated into ions in the same degree as any other neutral salt.

The process would therefore be equally successful if in place of ammonium some other cation were employed, whose bicarbonate is more soluble than sodium bicarbonate. In the case of ammonium, however, there is the special advantage that free ammonia can, on account of its volatility, again be easily recovered from the residual chloride by means of lime.

The chemical reactions, therefore, can be summarised in the following equations:—

$$NaCl + HNH_4CO_3 = NH_4Cl + NaHCO_3$$
$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$$
$$NH_3 + H_2O + CO_2 = HNH_4CO_3$$
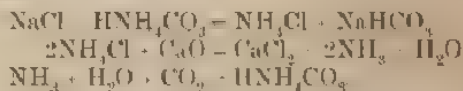
Besides sodium chloride, calcium oxide and carbon dioxide are used up. The latter are obtained from naturally occurring calcium carbonate or limestone, which decomposes into the two constituents on heating. Further, the sodium bicarbonate is placed on the market only in very small amount as such; the greater part is decomposed by heating into normal carbonate and carbonic acid $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$[1]

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[1] It is not easy to see why the decomposition of the calcium carbonate and of the ammonium chloride is not into one operation, for by heating the two together the carbonate would be obtained, which could then be dissolved in the solution of the salt. The carbonic acid from the decomposition of the sodium bicarbonate would be exactly sufficient to again precipitate such a carbonate from the solution. Probably technical difficulties have necessitated the indirect process.

The soda obtained in this way (Solvay process) is not only cheaper than by the Le Blanc method, but it is also considerably purer.

For special purposes, pure soda is obtained by precipitating the carbonate from a concentrated solution of the impure salt by means of carbon dioxide, washing this with cold water and converting it by strongly heating into the normal carbonate.

In analysis, sodium carbonate is employed for several purposes. On the one hand, it is used as a reagent for introducing carbanion, CO_3, into a given solution, since many carbonates are difficultly soluble in water, the respective cations will be precipitated by this addition. On the other hand, sodium carbonate is used for decomposing various salts at a red heat, more especially for decomposing silicates and rendering them suitable for analysis. For this purpose, it is mixed with about an equal weight of potassium carbonate. Such a mixture melts much more readily than either of the salts alone. This is another example of the mutual depression of the melting point (vide p. 477).

471. Sodium Phosphate.—Of the three sodium salts of ortho phosphoric acid, the best known is the disodium salt Na_2HPO_4, this is the salt meant when *sodium phosphate* is spoken of without further designation. It generally crystallises in large crystals containing $2H_2O$, which readily effloresce; with most of the other sodium salts, however, it shares the property of forming crystals containing different amounts of water, according to the temperature of crystallisation. Thus, more especially, a salt with $7H_2O$ is known which is formed at temperatures above 35, and is also formed by the efflorescence of the more highly hydrated salt.

At higher temperatures, the salt first loses its water of crystallisation, and then the unreplaced acid hydrogen is given off as water, and there is formed the *sodium salt of pyrophosphoric acid*: $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. This is the most convenient method of preparing a pyrophosphate, and from this pyrophosphoric acid (p. 368).

* The above reaction is of great historical interest. The change in the chemical reaction which accompanies the above transformation, led, of a necessity, to the conclusion that the nature of the acid had undergone an essential change by the ignition, and after Clark and Graham had subjected the chemical processes which take place to an exact analytical investigation, and had established the fact that these consist merely in a loss of water, it was possible for Liebig, on the basis of this result, to put forward the *theory of the polybasic acids*. For since at that time (1838) the methods for the determination of the molar weights had not yet been elaborated, all acids were formu for the sake of simplicity, as containing only one combining replaceable hydrogen. Liebig showed that the facts cou consistently and clearly represented by giving up this as writing, where necessary (more especially in those cas

salts can be prepared), the formulæ of the acids with two or more
combining weights of replaceable hydrogen. This method of formula-
tion received confirmation through the conception of molar weight,
which was subsequently developed.

The aqueous solution of disodium phosphate reacts feebly alkaline.
The reason of this has already been given (p. 368), the second
hydrogen of phosphoric acid is only slightly dissociated, and a certain
amount of hydrolysis therefore occurs in the solutions of the corre-
sponding salts.

In the laboratory, the solution of disodium phosphate is employed
to introduce phosphanion into reactions. By reason of the nature of
the dissociation of phosphoric acid, to which reference has just been
made, the solution of the salt contains, to a preponderating extent, the
ion HPO_4''. If, as is necessary for most of the precipitations, it is
desired to bring the ion PO_4''' into reaction, it is further necessary to
add a base, the hydroxyl of which can form water with the hydrogen
of the ion HPO_4'', and thereby convert it into PO_4'''. This transfor-
mation, it is true, takes place only to a small extent in the solution
itself; if, however, the ion PO_4''' is continuously removed from the
solution by the deposition of a solid salt, a fresh quantity must
always be formed in order to establish chemical equilibrium in the
solution, and the object aimed at will be attained. Usually ammonia
is the alkali added, because an excess of it does no harm, which is
sometimes not the case with an excess of caustic soda or potash.

If to a solution of the ordinary sodium phosphate the quantity of
caustic soda required by the equation $Na_2HPO_4 + NaOH = Na_3PO_4 +
H_2O$ is added and the solution evaporated, the *trisodium phosphate*
is obtained in hydrated octahedral crystals, which dissolve in water
with a strongly alkaline reaction. By addition of phosphoric acid
in accordance with $Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$, and evaporation,
monosodium phosphate is obtained which crystallises in two different
forms, each containing $1H_2O$. On being heated this salt passes into
the *sodium salt of metaphosphoric acid* : $NaH_2PO_4 = NaPO_3 + H_2O$.

The sodium salts of pyro- and metaphosphoric acids, which have
just been mentioned, are the most important salts of these anions.
While the pyrophosphate has only a limited application (in medicine),
the metaphosphate is largely used as a reagent in qualitative analysis.
It is obtained as a glassy mass by heating monosodium phosphate, and
does not crystallise when it is dissolved in water and the solution is
evaporated; at a red heat it has the property of dissolving many
metallic oxides, with production of a characteristic colour. In using
it, a small quantity is fused to a bead on a loop of platinum wire, and
to this is added a small quantity of the substance under investiga-
tion. The various heavy metals, more especially, give characteristic
colours in the "phosphate bead."

472. **Sodium Silicate** behaves quite similarly to potassium

licate, and is employed as *soda water-glass* (p. 470). Together with
ther silicates, it occurs both naturally (*e.g.* as *albite*) and as a manu-
 factured product; thus, for example, ordinary *glass* is a mixture of
sodium and calcium silicates.

473. **Sodium Borate**. Of all the salts of boric acid, a sodium
compound is the best known and the most largely used. This salt is
called *borax*, and has the composition $Na_2B_4O_7$; it is, therefore, the
sodium salt of tetraboric acid, $H_2B_4O_7$, which may be supposed formed
from four combining weights of orthoboric acid by the loss of $5H_2O$:

$$4H_3BO_3 - 5H_2O = H_2B_4O_7.$$

Borax is a salt which is not very soluble in water; at lower
temperatures it crystallises with $10H_2O$, above 56° with $5H_2O$. The
former, or more highly hydrated form, is distinguished as *prismatic*
borax from the less hydrated or *octahedral* borax. The relation exist-
ing between the two salts is similar to that between Glauber's salt and
anhydrous sodium sulphate (p. 491), only the octahedral borax is very
easily formed, even in its region of instability below 56°, if nuclei of
the prismatic form are excluded.

When heated, borax loses its water, first swelling up to a spongy
mass, and then, as the temperature is raised, forming a colourless glass
which, on cooling, solidifies in the amorphous condition.

This *borax glass* has, similarly to sodium metaphosphate, the pro-
perty of dissolving metallic oxides with production of distinctive
colorations, and is therefore used in qualitative analysis for the same
purpose as the latter salt. In the case of borax, however, the melting
point lies considerably higher, and the colours are also to some extent
different, so that the reactions in the borax and those in the phosphate
bead must be distinguished. To this solvent power for metallic oxides,
the application of borax in *soldering* is also due. Soldering consists
in uniting two pieces of metal together by fitting them to one another
and filling up the space which is left with an easily fusible metal in
the liquid form. In order that such a junction may hold, the liquid
metal must wet the surfaces to be united; this is, however, hindered
by the layers of oxide with which most of the metals become covered
when heated. When the borax melts, it covers the metal, and thus
prevents the access of atmospheric oxygen; it also dissolves the oxide
which is present, and thus renders the wetting by the liquid metal
possible. Borax is used in soldering with difficultly fusible, or *hard
solder* (a mixture of copper, zinc, and silver); with easily fusible *soft
solder* (tin and lead) there are used zinc chloride, ammonium chloride,
resin, or stearic acid, which have a similar action to borax.

474. **Sodium Acetate.**—*Sodium acetate*, $NaC_2O_2H_3$, $3H_2O$, is a
salt which is readily soluble in water, and melts at 58° in its water
crystallisation; after the addition of a small amount of we
fused product can be cooled down without crystallising.
liquid, which, if "nuclei" are excluded, will keep for y

periments on supercooling (p. 119) can be very conveniently performed, since, as a rule, no nuclei of the salt are present in the air, and the apparently spontaneous crystallisation does not readily occur.

In the laboratory, sodium acetate is often employed. It is chiefly used in analytical chemistry for the purpose of preparing solutions which have an acid reaction but contain a *very small concentration of hydrion*. Since several of the precipitates employed for analytical purposes are dissolved by strongly acid liquids, but are sufficiently insoluble in weakly acid ones, an artifice like this is of great importance.

The above object is attained by adding sodium acetate to the solution which contains hydrion, e.g. hydrochloric acid (or in which hydrion is formed in the intended reaction). The acetanion thus introduced into the solution combines with the greater portion of the hydrion present to form undissociated acetic acid, since acetic acid is a rather weak acid, and only a small amount of hydrion is left. If more hydrion is formed in the reaction, this undergoes the same transformation, always supposing that there is acetanion still present. The sodium acetate must, therefore, be added in sufficient excess.

475. **The Combining Weight of Sodium** has been determined in conjunction with that of silver and chlorine (p. 226) by ascertaining how much silver is necessary for the conversion of a definite amount of sodium chloride into silver chloride, or how much silver chloride can be obtained from a given amount of sodium chloride. In this way it has been found, Na = 23·05.

CHAPTER XXII

RUBIDIUM, CÆSIUM, LITHIUM, AND AMMONIUM

General.—To the two alkali metals, potassium and sodium, which occur very abundantly in nature, there are related three other elements which are found much more sparingly. One of these, lithium, has a smaller combining weight than the above mentioned metals, viz. 7·03. The other two, *rubidium* and *cæsium*, have a higher combining weight, viz. 85·4 and 133. In their chemical relations, the latter two are quite analogous to potassium, while lithium stands alone in the group, and its chemical analogues are rather to be found in the elements of the next group, that of the alkaline earth metals.

In view of this circumstance, it may be asked why lithium is so preferably classed along with these other metals. The complete answer to this can be given only after all the assumptions necessary for a comprehensive systematisation of the elements have been discussed. The decisive reason may be here given, viz. that lithium forms a *monovalent* ion, like the alkali metals, whereas the ions formed from the alkaline earth metals are all *divalent*. The specific heat and other relations are connected with this, and all favour the placing of lithium in the group of the alkali metals. It will also be found that deviations similar to those found in the case of lithium can be frequently and regularly observed.

In this chapter *ammonium* (p. 508) also has been placed, because it forms a monovalent cation NH_4, which is in many respects similar to potassium.

477. Rubidium and Cæsium.—After the foundations of *spectrum analysis* had been laid by Bunsen and Kirchhoff in 1860, the former proceeded to apply the new method to several substances. And, first, in the mother liquor from the salt wells at Durkheim, he found new spectral lines which did not belong to any of the elements hitherto known. In a masterly research · he separated the correspond-

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· Bunsen isolated 9 gm of rubidium chloride and 7 gm of cæsium chloride from 240 litres of mineral liquor, corresponding to 44,200 kgm. of mineral water.

ing substances and established the fact that two new alkali metals were present, which were especially similar to potassium. From the colour of their most pronounced spectral lines, he called them rubidium (red) and cæsium (blue).

The two elements were subsequently often observed, but always in very small amount. Rubidium is found most abundantly in the mother liquors from the Stassfurt potash salts, from which it is separated in the form of its difficultly soluble double salt with aluminium sulphate (alum). Cæsium compounds still remain very rare.

The chemistry of these two elements, so far as investigated, agrees perfectly with that of the potassium compounds. The corresponding salts are generally isomorphous, and exhibit similar solubility relations. More especially do these metals form difficultly soluble salts with the ions $PtCl_6''$, SiF_6'', and BF_4'; the acid salts of tartaric acid are also difficultly soluble. For this reason there are no methods known by which a tolerably sharp separation of these elements can be effected, and one has to be satisfied with incomplete separations based on slight differences in solubility, which must be frequently repeated before the object is approximately attained.

Thus from the previously concentrated mixture of the three chlorides, by the addition of hydrochloroplatinic acid, Bunsen separated a small precipitate which consisted of the less soluble salts of the two new elements mixed with the more soluble potassium platinochloride. By boiling this precipitate with small quantities of water and adding the portion which passed into solution to the original liquid, he obtained a less and less soluble platinum salt, which finally was almost free from potassium. The separation of rubidium and cæsium was effected by treating the carbonates, or the hydroxides, with alcohol

Metallic rubidium, which can be obtained by distilling the hydroxide with magnesium, has the density 1·5, melts at 38°, and at room temperature is very soft. It readily volatilises, and ignites spontaneously in moist air and also in dry oxygen. It dissolves in mercury, forming an amalgam, which behaves like potassium amalgam.

In oxygen, rubidium burns to a dark coloured dioxide, RbO_2, which dissolves in water, yielding the hydroxide with formation of hydrogen peroxide and oxygen. The hydroxide is obtained from the sulphate by precipitating the sulphanion with barium hydroxide.

Of the different salts of rubidium, nothing special has to be said

One peculiarity which is not found in an appreciable degree in the case of potassium, is the property possessed by rubidium and cæsium of forming compounds with the halogens, in which three or five combining weights of the latter to one combining weight of the metal are present; compounds, therefore, in which the metal appears as tri- or pentavalent. Such compounds with bromine or iodine are formed with especial ease. They are deposited as difficultly soluble crystalline pre-

on introducing the free
oxide.   Through these
to heavy metals thallium
ers, have also been ranked
rods are much more readily

and is still more readily

rds of the other alkali metals,
Arfvedson in 1817.   Elementary
by Bunsen and Matthiessen, by the

of all solid substances, its density
It is a silver white, somewhat
melt below 180, and does not
When heated in the air, it does not
200, and it then burns with a white,
of magnesium.   It decomposes water
formation of lithium hydroxide; the
less violent than with the other alkali metals
metals, lithium forms a monovalent, colour-
combine to form salts with all anions.   From
alkali metals, lithium is distinguished by its
readily soluble salts, which will be mentioned
is not capable of forming any but monovalent

Hydroxide is most easily obtained by decom-
ate with barium hydroxide.   On strongly con-
ation, lithium hydroxide, LiOH, separates out as a
which is readily soluble in water, although not so
potash or soda, but does not deliquesce in air.   The
however, essentially the same properties as those of caustic
soda, for lithium hydroxide is dissociated into its
LiOH', in almost the same degree as the other alkalis.
ounds of lithium with chlorine, bromine, and iodine are
ably soluble, and deliquesce in the air, since their satu-
tions have a smaller vapour pressure than the mean vapour
of the water in the air.   They dissolve in alcohol and in a
alcohol and ether.   Since the chlorides of the other alkali
almost insoluble in this mixture, use is made of this pro-
the separation of lithium from these.
Lithium fluoride, however, is very difficultly soluble in wate
Lithium nitrate and *sulphate* are readily soluble in water
Lithium Carbonate, Li$_2$CO$_3$, is difficultly sol
100 parts of water dissolve only about one part c
other hand, lithium *bicarbonate* is much more easi

acid, however, which is split off is immediately oxidised by the atm
spheric oxygen (p. 237), free iodine is formed, and the same series of
reactions occurs over again. The salt can be preserved by excluding
air and moisture.

487. **Ammonium Nitrate.**—This salt has already been mentioned
on a former occasion (p. 345), since on account of its decomposition
into nitrous oxide and water on heating, it is used for the preparation
of that gas. It is obtained as a very soluble salt by neutralising nitric
acid with ammonia or ammonium carbonate, and evaporating. When
thrown on red hot charcoal, it decomposes with production of flame
alone, or mixed with charcoal, it can be made to explode, and it is
therefore used in the preparation of *explosives*. These are made
with difficulty, and can therefore be used without danger. Since the
substance is converted completely into gases and vapours, the explosive
effect is an advantageous one, especially as the nitrous oxide formed
gives out a considerable amount of heat on decomposing (p. 344)

488. **Ammonium Nitrite**, NH_4NO_2, is of interest on account of
its ready decomposability into water and nitrogen (p. 345); in the free
state it is known only as a deliquescent and decomposable crystalline
mass.

489. **Ammonium Sulphate**, $(NH_4)_2SO_4$, is isomorphous with
potassium sulphate, but is much more readily soluble in water than
the latter. Similarly to potassium sulphate, it forms various double
salts, more especially with the divalent sulphates of the magnesium
group and with the trivalent sulphates of the aluminium family.
The solution is somewhat more strongly dissociated hydrolytically
than that of ammonium chloride. If the solid salt is heated, it loses
ammonia and passes into the acid ammonium sulphate, NH_4HSO_4;
this is a reaction which is peculiar to the normal ammonium salt of
all polybasic acids.

490. **Ammonium Phosphates.**—Of the three possible ammonium
phosphates, only the first two are known, the mono- and the di-
ammonium phosphate, since the normal salt decomposes so readily
into ammonia and diammonium phosphate that it does not keep.
The salts are of no special importance.

A salt which is better known is sodium ammonium phosphate,
$NaNH_4HPO_4$, $4H_2O$, or *microcosmic salt*. It is used instead of sodium
metaphosphate for blowpipe experiments, since it passes into the latter
salt on heating. The decomposition takes place according to the
equation $NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3$. Since this decomposi-
tion is accompanied by a considerable swelling up of the salt, it is
more convenient not, as is usually done, to first prepare the "phosphate
head" on the platinum wire immediately before the experiment, but
to directly employ sodium metaphosphate. The name *microcosmic salt*
is due to the fact that the compound is formed in the evaporation of
human urine (decomposed by putrefaction). This liquid excretion of

useless constituents of the organism was regarded by the alchemists
extract of the human microcosm.

491. **Ammonium Carbonate.**—Normal ammonium carbonate is
unstable, since it undergoes with great readiness the general
composition of the ammonium salts of polybasic acids. On the
other hand, the acid salt NH_4HCO_3 is very stable, and scarcely smells
ammonia. It crystallises from solutions of ammonia which have
been saturated with carbon dioxide. The two salts combine with
another to form a double salt, the so-called ammonium sesqui-
bonate $(NH_4)_2CO_3 + 2NH_4HCO_3$, which forms the chief constituent
commercial ammonium carbonate. The latter usually also con-
ns *ammonium carbamate* or the ammonium salt of *carbamic acid*
399), which is produced from the normal carbonate by loss of
ter: $(NH_4)_2CO_3 = NH_2OCONH_2 + H_2O.$

492. **Ammonium Sulphide.**—The two compounds which sulphu-
ated hydrogen can form with ammonium are largely employed in the
laboratory. They are prepared by passing sulphuretted hydrogen gas
through a strong solution of ammonia. With excess of sulphuretted
hydrogen, ammonium hydrosulphide, NH_4HS, is formed in the solution;
to this is added as much ammonia as was originally taken, a solution
of ammonium sulphide, $(NH_4)_2S$, is obtained. The latter solution does
not contain solely ammonium sulphide and its ions, any more than the
corresponding compound is alone contained in the solution of the
lkali sulphides (p. 466); on the contrary, hydrolysis proceeds further
in this case than in that of the latter, for we are here dealing with the
salt of a weak base with a weak acid. For those reactions, however,
in which sulphidion S'' is consumed, the actual condition of the solution
is of comparatively little importance, since the sulphidion which is used
up in the reaction can be produced afresh in proportion as it passes
out of the solution.

Both the above salts can be obtained in the solid state by mixing
sulphuretted hydrogen and ammonia gas in the necessary propor-
tions: $NH_3 + H_2S = NH_4HS$ and $2NH_3 + H_2S = (NH_4)_2S$. In this
way, crystalline masses are obtained the vapour density of which
shows that, on vaporisation, they again decompose into their com-
ponents. The sulphide is exceedingly readily volatile, the hydro-
sulphide less so.

* In the case of ammonium hydrosulphide, thorough investigations
have been made concerning the equilibrium between the solid salt and
its vapour. If we denote the concentrations of the ammonia and of
the sulphuretted hydrogen by a and b respectively, and by c the con-
centration of ammonium hydrosulphide in the vapour (this is, indeed,
very small but not zero), then, in accordance with the general equation
of equilibrium (p. 330), we have the relation $ab : c = k$. The concen-
tion of the undissociated ammonium hydrosulphide is depende
on the temperature, since, according to Dalton's law, the v

sure of a given substance remains the same whether other substances are present in the gas space or not.   For each temperature, therefore, the product ab must also be constant.   It is a case of an equilibrium, therefore, which is perfectly similar to that between a solid salt and its partially ionised solution (p. 447).   As a matter of fact, also, the following peculiarities were found :—

(a) If there is no excess of one of the components in the gas space ($a = b$), a definite dissociation pressure is established which is dependent only on the temperature, and not on the relative amounts of solid substance and vapour.

This follows from the equation, for if $a = b$, the equation assumes the form $a^2 = kc$, and k as well as c depends only on the temperature.

(b) Less of the solid substance evaporates into a space in which ammonia or sulphuretted hydrogen is already present ; the effect of equal excesses of the two gases is equal.   This also corresponds to the equation, for the expression abc is symmetrical in respect of a and b.

* The equilibrium of ammonium sulphide would necessarily be represented by an equation of the form $a^2b\,c = k$, because two moles of ammonia react with one mole of sulphuretted hydrogen.   The decomposition of ammonium sulphide, however, does not take place in such a way that the two gaseous components are formed, but in such a way that ammonium hydrosulphide is produced along with free ammonia.   The conditions of equilibrium become thereby complicated, and will not be discussed here.

The aqueous solution of ammonium sulphide rapidly becomes coloured yellow in the air, because the sulphuretted hydrogen which is split off by hydrolysis is oxidised by the atmospheric oxygen (cf. p. 278); the sulphur which is formed dissolves in the excess of ammonium sulphide to form polysulphides, corresponding to the alkali polysulphides (p. 467).   A tetra- and a heptasulphide of ammonium $(NH_4)_2S_4$ and $(NH_4)_2S_7$, have been prepared in the *solid* state.

In the laboratory, ammonium sulphide is used for the precipitation of those metallic sulphides which are dissolved by free acids.   The theory of these precipitations has already been given (p. 277).   Potassium and sodium sulphide have the same action, but ammonium sulphide is preferred, because an excess of it can be more easily removed from a solution.

Yellow ammonium sulphide is used for dissolving those metallic sulphides whose higher sulphur compounds can pass into thio-acids and form soluble ammonium salts.   Tin sulphide is an example of this.   Further information on this point will be given under the respective metals.

Besides being used for obtaining sulphur compounds, ammonium sulphide is also used as a reducing agent, especially in organic chemistry.   The action depends on the corresponding properties

sulphuretted hydrogen (p. 278); ammonium sulphide has the advantage that the reagent can be used in a much more concentrated form than the slightly soluble sulphuretted hydrogen. Hydrogen is used up in the reaction, the sulphur is precipitated, and ammonia is liberated. Fresh sulphuretted hydrogen can then be passed into the solution, if it is necessary to continue the reduction.

CHAPTER XXIII

CALCIUM

493. General Remarks on the Alkaline Earth Metals.—The metals of this new group are distinguished from the alkali metals, essentially by their power of exclusively forming *divalent cations*. That is seen from the fact that, *e.g.*, the amount of calcion which can combine with a given amount of chloridion, does not depress the freezing point of the aqueous solution by the same amount as the chloridion, but only by half as much. One molar weight of calcion, therefore, combines not with *one* but with *two* molar weights of chloridion, and for this reason it must be regarded as divalent.

* Since the different ions cannot be handled separately, the above result was obtained *indirectly*. If very dilute solutions of potassium chloride and of calcium chloride are prepared, in which the concentrations of the chloridion are the same, and the freezing points are determined, the depressions of the latter are not equal but are in the ratio of 4 . 3. Since, in the case of potassium chloride, an equal share of the depression is due to each of the ions,[1] the share of the chloridion in the solution of calcium chloride must also be put equal to two, and the calcion has only the effect one, *i.e.* acts half as strongly as the potassion. From this the above conclusion follows.

Other differences, although not so decisive, are found in the *solubility relations* of the salts. Thus, for example, the normal carbonates and phosphates of the alkaline earth metals are very difficultly soluble in water; indeed it is only the alkali metals that can form readily soluble salts with the ions carbanion and phosphanion (and with a series of similar ions). It has, however, just been specially mentioned that in this respect lithium forms a transition.

The metals of this group are less sensitive to free oxygen and to oxygen compounds than the alkali metals; they are also much less readily fusible and volatile than the latter. Here also the same gra-

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[1] This is seen from the fact that one mole (= 74·6 gm.) of potassium chloride gives a depression of the freezing point which is twice as great as that given by an mole of an undissociated substance.

516

ulphuretted hydrogen (p. 278); ammonium sulphide has the advan-
ge that the reagent can be used in a much more concentrated form
ian the slightly soluble sulphuretted hydrogen.   Hydrogen is used
p in the reaction, the sulphur is precipitated, and ammonia is
berated.   Fresh sulphuretted hydrogen can then be passed into the
»lution, if it is necessary to continue the reduction.

The reason of this is that oxalic acid is an acid the strength of electrolytic dissociation of which lies between that of hydrochloric acid and of acetic acid   If calcium oxalate is brought into contact with water, a very small quantity of the precipitate dissolves. acetic acid is added to the liquid, it contains such a small amount of free hydrion that only an extremely slight change takes place in the chemical equilibrium, in such a sense that quite a small quantity of the oxalanion unites with hydrion to form undissociated oxalic acid, or the monovalent hydro-oxalanion, C_2O_4H', the consequence is a very small increase in the amount of salt passing into solution.   Since it is, the solubility of calcium oxalate is very slight, this increase is of no account analytically.

The case is different when a strongly dissociated acid, like hydrochloric acid, is added.   A large amount of hydrion is then introduced into the solution, and, accordingly, a comparatively large amount of oxalanion, C_2O_4'', disappears, owing to the formation of HC_2O_4' and $H_2C_2O_4$, and must be replaced by more calcium oxalate passing into solution.   Accordingly, much more of the precipitate will be dissolved and with sufficient amount of hydrochloric acid the whole precipitate passes into solution.

For this reason, in precipitating calcion with oxalanion, one does not use a solution of *free oxalic acid*, whereby the detrimental hydrion would be introduced into the solution, but *ammonium oxalate* is employed.   If the solution itself is strongly acid, the excess of hydrion can be removed by addition of *sodium acetate*, acetanion, being the ion of a weak acid, unites with the greater part of the hydrion to form undissociated acetic acid, and only a harmless amount of hydrion is left behind.

According to the temperature employed, the precipitate of calcium oxalate contains various amounts of water of crystallisation, and can not, therefore, be weighed as such in the quantitative determination of calcium.   It is, therefore, heated either gently to convert it into calcium carbonate ($CaC_2O_4 = CaCO_3 + CO$), or, since some calcium oxide can thereby be readily formed, it is better to heat it to a bright red heat, whereby it is completely converted into *calcium oxide*.

Calcium oxalate is also found as a constituent of certain urinary calculi and very widely distributed in almost all plants; in the cells of the latter the comparatively large, transparent octahedra of hydrous calcium oxalate, which have the appearance of an envelope, can be readily recognised under the microscope.

512   Calcium Carbide — If carbon acts on lime at a very high temperature, there occurs the reaction $CaO + 3C = CaC_2 + CO$.   The compound CaC_2, which is formed is called *calcium carbide*, and has been manufactured for some years in very large quantities for conversion into acetylene (p. 410)

The reaction is carried out in the electric furnace, but the process

nothing to do with electrolysis, the current serving only to pro-
... the requisite high temperature, and to yield the large amounts
... energy which the
... tion requires. In
... 113 an experi-
... tal electric furnace
... represented, formed
... ply of refractory
...
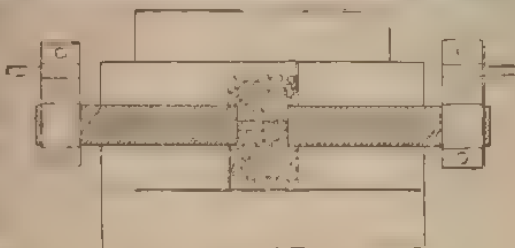
Pure calcium car-
... forms almost
... colourless crystals.
... commercial pro-

Fig. 113.

... appears as a black-grey mass of irregular lumps, having the
... characteristic smell of phosphoretted hydrogen, which, however, is
... only to impurities. Its density is 3.22, and it does not melt
... a white-heat.

The most important reaction of the carbide is that it is decom-
posed by water with formation of calcium hydroxide and *acetylene* :
$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. In this reaction a considerable
amount of heat is developed, so that if water is allowed to come into
contact with a comparatively large quantity of carbide, the tempera-
ture can rise to a red-heat. The acetylene is, however, decomposed
under such conditions, and a poorly luminous gas is obtained. Those
acetylene generators, therefore, are the best in which the carbide falls
into a comparatively large quantity of water, or in which the rise of
temperature is otherwise avoided.

The problem of making an automatic acetylene generator, which
appears capable of simple solution on the principle of the apparatus
described on p. 87, has in reality turned out to be very difficult. This
is due, on the one hand, to the fact just mentioned, and on the other
hand, to the fact that calcium carbide reacts powerfully even with water
vapour, so that the so-called *after-evolution* of gas, i.e. a constant evolution
of gas even when the apparatus should be at rest, is difficult to avoid.

The detrimental effect of moderate heat on acetylene can be
easily shown by allowing the gas to pass through a horizontal tube
before entering the burner. So long as the tube is cold, the flame
burns very brightly, but so soon as it is heated even to a dark red
heat the flame becomes almost non-luminous, and charcoal is deposited
in the tube.

If, during the interaction between lime and carbon, nitrogen
from the air, is allowed access, a compound, *calcium cyanamide*, $CaCN_2$,
is formed. When this is treated with hot water the nitrogen is split
off as ammonia $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. The same reaction
takes place slowly in the cold, so that the substance can be used as a
nitrogen manure. (Cf. p. 489.)

513. Calcium Silicate and Glass.   Silicates of calcium occur in the pure state in nature, forming an important minerals which have but a slight distribution (*wollastonite*).   Combined with other silicates, however, calcium silicate is a very frequent constituent of the naturally occurring minerals.

As a chemical product, also, calcium silicate itself is of no importance, but is of great importance when mixed with the silicates of the alkali metals.   These mixtures constitute *glass*, the well known resistant and transparent material which finds an application in all departments of daily life, in the manufactures, in art, and in science.

Glass is a mixture of potassium or sodium silicate and calcium silicate.   This is the composition of ordinary window glass or of glassware.   For special purposes, still other metal oxides are used, and also phosphoric and boric acids in place of silicic acid.

The chemical composition of good glass agrees approximately with the formula $A_2CaSi_6O_{14}$, where A signifies potassium or sodium or both.   Ordinary glass, however, generally contains less silicic acid, since it is then more easily fusible.

Glass is amorphous, as is shown by its isotropic nature and the absence of a definite melting point.   In certain glasses there is a tendency for some portions to separate out in the crystalline state; this is known as *devitrification*, and it is endeavoured to avoid this condition by a suitable change in the proportions of the mixture. All the same, devitrification occurs in the case of almost all glasses when they are maintained for a long time at a temperature near the point of softening, but with good glass the process takes place with extreme slowness.

Whilst alkali silicate is fairly readily dissolved by water, glass is very resistant to this.   It is attacked least of all by acid solutions; pure water attacks it more strongly, and alkaline solutions most strongly of all.   By exposure for some time to the action of steam, the surface of glass vessels becomes less easily attacked.   Moreover, the resistance of the glass depends very largely on its composition; it is all the less the poorer the glass is in silicic acid and the richer it is in alkalis.   Further, the remarkable behaviour has been discovered that glass which contains potash or soda *alone*, is much more resistant than glass which contains both alkalis together.

* By reason of the inclination towards economy of fuel, it had formerly become a custom in glass works to manufacture a readily fusible glass, rich in alkali, so that the bad and small resistant character of such glasses became a source of distress.   The scientific investigations which were in consequence carried out, some of which have been mentioned above, at once led to a suitable adjustment of the factors which must be taken into account for manufacturing purposes, and at the present time there is produced at many places

especially at Jena, a glass for apparatus which is considerably superior in quality to the best sorts of glass previously made.

The action of water on glass consists in free alkali and alkali silicate passing into solution, a hydrated silicate containing less alkali being left. This action increases very rapidly with rising temperature, and above 200° no glass withstands the action of water.

In the *manufacture of glass*, one starts with silicon dioxide (quartz sand) potassium or sodium carbonate, and calcium carbonate. The components, mixed in the proper proportions, are first maintained for some time at a moderate red heat; the silicates are thereby formed, if no fusion, only sintering, occurs. This is done in order that the carbon dioxide may escape without the mass being thrown out of the vessel by the evolution of gas. The "frit" is then fused at a higher temperature, and is maintained at such a temperature for a sufficiently long time to allow the gas bubbles to escape, and the undissolved pieces of the mass to sink to the bottom.

If the glass is to be worked up by pouring into moulds, it may be used in the above condition of a thin liquid. Generally, however, the glass is "blown," and for that purpose it must be rendered more viscous by lowering the temperature. The blowing of glass is a shaping of it with the help of *surface tension*. A certain amount of the liquid glass is taken up with an iron tube, the "blow pipe," and is blown up like a soap-bubble. The fundamental form which is obtained is therefore a hollow sphere; under the action of gravity, of centrifugal force, and especially by suitably heating and cooling different parts of the object, very various forms can be produced.

For many pieces of apparatus, especially when small and complicated, the glass is worked *before the blow pipe*, after it has been brought into the form of *tubes* of various thickness and width in the glass-works. These tubes are obtained by first blowing a bulb, then fusing an iron rod to a point diametrically opposite to the blow pipe and slowly separating the two points of attachment from one another. A much-elongated ellipsoid is formed, the middle portion of which does not deviate materially from a cylinder. In working before the blow pipe the same aids are employed as in the works, viz. surface tension and suitable heating.

Moulded objects must be "annealed," and this must be all the more carefully done the thicker and larger these objects are. The annealing consists in allowing the temperature of the glass to sink only very slowly. Quickly cooled glass contains internal strains, which arise in the following manner. In rapid cooling, a low temperature is soon established at the surface, and the outermost layer solidifies while the interior is still very hot. The external volume of the lump corresponds, therefore, to the volume possessed by the interior portion at the high temperature; when the mass has become quite cold, the interior tends to contract, and thereby exerts on the

particular, it is independent of the proportions in which the two solid substances, calcium carbonate and lime, are present; it is also independent of the relative amounts of the solid and gaseous phases.

* This follows as a necessary consequence from the phase law. There are two components, lime and carbon dioxide, from which all the phases present can be compounded. Since there are three phases present, viz. carbon dioxide, lime, and calcium carbonate, there is only *one degree of freedom, i.e.* to each temperature there corresponds a perfectly definite pressure, and the amounts of the phases have no influence.

* The same follows from the law of mass action. If we call the concentration of carbonate, oxide, and carbon dioxide c, l, and d respectively, we obtain the equation $l \cdot d = k \cdot c$, in which k, the equilibrium constant, is a function of the temperature. In this equation, however, the concentrations of the solid substances, c and l, are constant, and consequently d must be a function only of the temperature.

As an examination of the table shows, the " burning " of lime by mere heating cannot be carried out under a temperature of 812°, since it is not till this temperature that the pressure of the carbon dioxide reaches one atmosphere and the escape of gas is assured. Since, however, this equilibrium depends not on the absolute pressure but only on the partial pressure of the carbon dioxide, the decomposition can be carried out at a much lower temperature by keeping the partial pressure of the carbon dioxide sufficiently low. This can be done by allowing another gas, most simply air, to stream over the heated carbonate; at each moment, then, there escapes (at most) so much carbon dioxide that the partial pressure corresponding to the particular temperature is established.

The great similarity which this phenomenon bears to that of the boiling and evaporation of volatile liquids, is easily seen. The temperature of 812° is, so to say, the boiling point of calcium carbonate.

The use of lime for *mortar*, which has already been mentioned several times, depends on the converse change into calcium carbonate. Mortar is a mixture of lime, sand, and water; in using it, the stones which have to be cemented together are moistened with water, a layer of mortar is introduced between them, and the whole is left to the influence of the atmosphere. By means of the carbon dioxide which the latter contains, the calcium hydroxide is slowly converted into carbonate, water being thereby set free: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. The crystals of carbonate, which are slowly formed, unite with one another and pass partly into the pores of the stones, the solubility of the lime enabling a certain, although small, amount of it to get in there. In this way the well known firm cementing together is gradually produced, and becomes firmer as time goes on, since even in very old mortar there is usually a certain amount of hydroxide present.

The fact that *water is set free* in the hardening of mortar under the

CHAPTER XXIV

MAGNESIUM

General.—Magnesium bears the same relation to calcium as sodium does to potassium. This relation finds expression not only in the values of the combining weights, but also in the similarities of the other members of the group. This is particularly well seen in the fact that magnesium is of more frequent occurrence than calcium, and that, in its properties, it differs from calcium more than the latter does from the corresponding elements of higher combining weight, strontium and barium.

That an elementary metal is present in the magnesium salt, was accepted by Davy as indubitable from the time that the corresponding fact was recognised in the case of potassium and sodium. Bunsen, however, was the first to prepare the metal itself. He obtained it by the electrolysis of the fused chloride.

The electrolysis can be performed in the lecture by employing fused carnallite as electrolyte and using the apparatus represented in Fig. 114. The partition and the prolongation of the crucible are of asbestos mill board, the cathode is a piece of iron wire, and the anode a thin arc-carbon. The strength of the current is about 3–10 amperes.

Magnesium is now manufactured in very large amount by electrolysis, and is used for various purposes. It is a white, rather tough metal, which keeps fairly well in the air; it is scarcely attacked by cold water, but in boiling water it slowly evolves hydrogen. In dilute acids it very rapidly dissolves, with energetic evolution of hydrogen. It melts at about 759°, and volatilises at a bright white heat.

Heated in the air, magnesium burns with a very bright, white flame, which is largely made use of. For example, instantaneous photographs can be easily taken by magnesium light. For this purpose magnesium is used in powder form, and is either blown
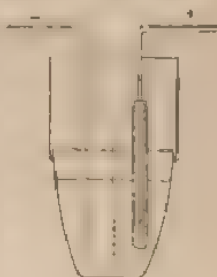
carbonate which is formed has, by reason of its slight solubility no
action on free iodine, whereas potassium carbonate would partly convert
free iodine into iodide and iodate, i.e. would to a certain extent hinder
the formation of free iodine.

503. Calcium Fluoride.—Unlike the other halogen compounds
of calcium, *calcium fluoride*, CaF_2, is very difficultly soluble in water.
The salt forms a widely distributed mineral which is known by the
name of *fluor-spar*. It crystallises in cubes and in other forms of the
regular system, is colourless and transparent in the pure state, but,
owing to the presence of impurities, is generally coloured in various
bright tints.

The name fluor-spar is derived from its application in metallurgical
work for rendering the slags which are then formed, readily fusible.
This action depends on the general fact that the freezing point of a
liquid is depressed by the solution in it of foreign substances; it is of
course, of no importance for this action whether the freezing point is
at 0 or at 1000. The element fluorine, also, has received its name
on account of its preparation from fluor-spar.

* Another name which is connected with this is *fluorescence*, which
is used to designate the property possessed by certain substances of
changing incident light into light of (generally) greater wave-length.
This property was first investigated with some degree of thoroughness
in the case of certain kinds of fluor-spar, but the property is a very
frequent one, and is more strongly developed in some other substances
than fluor-spar.

Fluor-spar is the most important starting substance for obtaining
hydrofluoric acid and the other fluorine compounds. Even at the
present time large quantities of it are used directly for the purpose of
etching glass; the salt is mixed with concentrated sulphuric acid, and
the articles to be etched are exposed to the action of the vapours of
hydrofluoric acid which are evolved.

504. Calcium Nitrate, $Ca(NO_3)_2$, is being unceasingly formed
through the activity of the nitrifying bacteria (p. 467) in the soil, since
calcium is the most widely distributed of the salt-forming elements
which have here to be taken into account. In localities where the
formation of nitrate is abundant, such as in the neighbourhood of cow-
houses, the anhydrous salt sometimes crystallises out during dry
weather on the stone walls in the form of thin needles which have
almost the appearance of mould. As a rule, no great accumulation of
the salt occurs in the soil, since the nitrates formed are at once taken
up by plants.

The pure salt is very soluble in water, and, at medium tempera-
tures, crystallises with $4H_2O$. It, also, is capable of forming a tolerably
large number of different hydrates.

505. Calcium Sulphate, $CaSO_4$, is difficultly soluble in water; it
occurs very widely distributed in nature, and, after calcium carbonate

e most abundant salt of calcium. It occurs in two forms It
s most frequently as *gypsum*, in monoclinic, sometimes very large
transparent crystals with two moles of water of crystallisation ;
more rarely as *anhydrite*, in anhydrous, rhombic crystals. The
bility of these two forms is different, gypsum being more difficultly
le than anhydrite. In the presence of water, therefore, the latter
ne less stable form and changes into gypsum ; in this case, also,
presence of a "nucleus" of the more stable form has an essential
ence on the process.

The solubility of gypsum amounts to about 2 gm. per litre ; as the
erature rises, the solubility first increases, reaches a maximum at
and then decreases. On being heated to 120°, gypsum loses ¾ths
s water of crystallisation,[1] and the transparent crystals are thereby
erted into a chalk white powder, which has a manifold application
r the name of *plaster of Paris* This depends on the fact that the
der again takes up its water of crystallisation in contact with water ,
ong needles of the crystallised gypsum are thereby again formed,
hese, intergrowing with one another, form a compact mass. This
nal is made use of for moulding objects for use and works of art,
plastering walls, for bandages in surgery, etc. The hardening of
er of Paris which has been slaked with water takes place in about
arter of an hour, and is accompanied by a feeble but appreciable
of temperature.

Plaster of Paris is a chemical compound, a *hemihydrate*, $2CaSO_4$,
, which can be obtained in crystals by allowing ordinary gypsum to
l with concentrated nitric acid and then evaporating off the latter.

If gypsum is heated above 300°, it loses all its water, and no
ger sets with water It is then said to be "*dead burnt.*" In this
dition it is probably the same as the natural anhydrite, which also
s not combine with water in measurable time. If, however, gypsum
dehydrated at a low temperature over sulphuric acid, it can part with
its water of crystallisation without losing its power of setting.
s peculiar difference in behaviour is probably due to the presence,
gypsum dehydrated at low temperatures, of "nuclei," or traces of
decomposed hydrate, which in the case of dead burnt gypsum have
destroyed by the high temperature employed.

The following experiment illustrates this view If effloresced
uber's salt, in which "nuclei" are still present (p. 493), is mixed
h a little water, the mixture at once hardens to a solid mass of
uber's salt ; but if the powder is previously heated, so that the
lei are destroyed, and is then mixed with water, avoiding the
oduction of nuclei from without, no solidification occurs, but a paste
rmed consisting of a saturated solution of the anhydrous salt al
undissolved substance.

The vapour pressure of the water of crystallisation amounts to one atm
but the temperature must be raised to 120 to obtain a rapid decompositi

by heating without undergoing decomposition, for it loses hydrogen chloride, and magnesium oxide or a basic chloride is formed MgCl₂ + H₂O MgO + 2HCl. This reaction is made use of on the large scale for obtaining hydrochloric acid; in recent times this has become of greater importance from the fact that the formerly very abundant source of hydrochloric acid constituted by the Le Blanc method of manufacturing soda is beginning to fail. For this reason magnesia is used even in those alkali works which use the ammonia process for the decomposition of the ammonium chloride which is formed (p. 310), because magnesium chloride can be much more easily decomposed by steam than calcium chloride.

Magnesium chloride forms double salts with potassium or ammonium chloride, of which that with potassium chloride, $MgCl_2 . KCl . 6H_2O$, called *carnallite*, is the most important naturally occurring potassium salt. It is found in large quantities at Stassfurt and in other parts of Middle and North Germany, and is separated into its components by crystallisation in the heat. The rather complicated equilibrium relations which exist in such solutions, show that in general it is most expedient to work at high temperatures. For example, if carnallite is heated without the addition of water, it liquefies at 176°, and deposits the greater part of the potassium chloride in the solid state ; on cooling down, almost all the rest of the potassium chloride crystallises out as carnallite, and the magnesium chloride remains in the mother liquor.

The greater part of the magnesium chloride produced in the manufacture of the potash salt finds no application at present, but is turned into the river channels. It is to be desired that some technically practicable means may be discovered to put an end to this, from various points of view, detrimental waste.

519. **Magnesium Sulphate,** $MgSO_4$, is a substance well known under the name of *Epsom salts ;* it has a bitter taste, due to magnesia. It usually crystallises in rhombic crystals with $7H_2O$. It can however, occur in a number of other forms containing from $12H_2O$ to $1H_2O$, according to the temperature. Mono-hydrated magnesium sulphate occurs in the Stassfurt salts as *kieserite.* Dissolved magnesium sulphate is a constituent of many mineral waters,[1] to which it imparts a bitter taste, and which are known as magnesia waters. The action of Epsom salts in the intestine is quite similar to that of Glauber's salt, but a specific action is also exerted.

Magnesium sulphate unites with potassium or ammonium sulphate to form double salts of the formula $MgSO_4 . K_2SO_4 . 6H_2O$. The potassium compound has the mineralogical name *schoenite,* and is used as a potash manure.

520. By **double salt** there is understood a crystalline compound of several normal salts with one another. This combination casts

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[1] The name Epsom salts is derived from the occurrence of this salt in the mineral waters at Epsom. Tr.

...ally only in the solid state, for the aqueous solutions of these ...salts exhibit exactly the same reactions as belong to the ions ...single salts, and no reactions which could belong to any new ...The determination of the molar weights of these aqueous solu-...tions, shows that no combination between the single salts exists ...appreciable extent, for the depression of the freezing point, for ...ple, is equal to the sum of the depressions which are caused by ...single salts under the same conditions.

...his holds in the first instance for dilute solutions. In concen-...solutions certain phenomena point to combination existing in ...to a certain, although not large, extent.

...a rule, double salts are less soluble in water than the com-...ts. If the difference is great, these double salts readily crystal-...from solutions in which the components are brought together. If, ...ver, the solubilities are of the same order, it depends on the tem-...ature and the relative amounts whether crystals of the double salt ...one of the components are obtained on concentration. In some ...double salts can be obtained only from solutions which contain a ...excess of one of the components. This holds, for example, for ...crystallisation of carnallite, which is formed only from solutions ...ining a large excess of magnesium chloride.

Double salts are generally so constituted that the single salts have ...on, either the cation or the anion, in common. Double salts with ...nt cations and anions do indeed occur, but they are more seldom. ...uble salt of this nature is kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$, which occurs ...sturt.

The *complex salts* must be distinguished from the double salts. ...the double salts, they can be formed by the union of two simple ...but their reactions in solution differ from those of the latter, ...h shows that new substances (ions) are formed. Further infor-...on concerning this interesting class of compounds will be given ...when we come to describe some complex salts (v. Chap. XXVII.) ...alkali and alkaline earth metals do not form any complex cations. ...The *isomorphous mixtures*, also, must be distinguished from the ...ble salts. They arise by the crystallisation of isomorphous salts ...a common solution; thus, for example, a mixed solution of ...um and potassium sulphates, or of sodium sulphate and sodium ...te, deposits crystals whose composition also appears as the sum of ...two components. These mixtures differ from the double salts in ...fact that their components are not, or are only accidentally, present ...combining proportions, and in the fact that *their composition varies* ...*ersely with the composition of the solution* from which they are ...ted. Their composition, therefore, cannot be represented by an ...nary chemical formula, but only by one with indefinite or con-...usly varying coefficients. They are usually written in the form ...Rh_2SO_4, and $Na_2(S,Se)O_4 \cdot 10H_2O$, the elements which replace one

another in indefinite proportions being placed in brackets and separated by a comma.

The double salts, however, are always compounded in combining proportions, and can, therefore, be represented by a chemical formula with definite, integral coefficients.

521   **Magnesium Carbonate**, $MgCO_3$, is a salt very difficultly soluble in water, which occurs in nature in large masses. As a mineral it is called *magnesite*, and crystallises in rhombohedra which are isomorphous with those of calc-spar.

When aqueous solutions containing magnesia and carbonic acid are mixed, a white, gelatinous precipitate is deposited, and carbon dioxide is evolved at the same time. This precipitate is not pure magnesium carbonate, but a varying mixture of carbonate and hydroxide. The higher the temperature and the greater the dilution, the greater is the amount of hydroxide and the less that of the carbonate contained in the precipitate. Washed with water and dried at a low temperature, this basic magnesium carbonate is placed on the market in the form of a light and loose powder, and is used in medicine as a mild alkali. It is called *magnesia alba*.

* The cause of this reaction is found in the *hydrolysis* which the carbonates undergo, and in the small solubility of magnesium hydroxide. In the aqueous solutions of calcium carbonate, also, hydrolysis occurs, and the ions HCO_3 and OH' are formed from carbanion, CO_3'', under the action of the water. Since, however, calcium hydroxide is much more soluble than the carbonate, the solubility product of the former is never reached, in spite of the presence of hydroxyl; and although the solution reacts alkaline, it deposits no hydroxide. In the same way, when the ions Ca', CO_3'', HCO_3', and OH' come together, as happens in the precipitation of a calcium salt with a soluble carbonate, the solubility product of the calcium carbonate is much sooner reached than that of the hydroxide; the precipitate, therefore, in spite of the hydrolysis which occurs, consists of normal carbonate. On the other hand, in the case of magnesium, the solubility product of the hydroxide is under such conditions, reached about the same time as that of the carbonate.

The normal carbonate can be prepared from the basic salt by suspending the latter in water and passing in carbon dioxide. After some time crystalline crusts of the hydrate, $MgCO_3 \cdot 3H_2O$, are formed. On being treated with much water, especially in the heat, it again passes into the basic hydrate.

Magnesium carbonate forms various double salts with the alkali carbonates. One of these, $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$, is deposited when carbon dioxide, under pressure, is passed into a solution of potassium chloride containing magnesium carbonate in suspension; magnesium chloride is formed at the same time and remains in solution. When this double salt is treated with steam under pressure, it decomposes

d, except olivine, contain more silicon dioxide than corresponds to e composition of an orthosilicate. They are distinguished by being a peculiarly soft and easily worked nature, accompanied by a great sistance to high temperature, and on this depend their applications. hey are mostly fairly readily decomposed by sulphuric acid.

525. Magnesium Nitride.—Magnesium nitride, Mg_3N_2, is obined as a yellowish, porous mass by heating metallic magnesium incandescence in nitrogen or ammonia gas. It is decomposed ith energy by water, with formation of ammonia and magsium hydroxide: $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$. In this way amonia can be obtained from free nitrogen (p. 351); for practical irposes, however, the method is still too expensive.

CHAPTER XXV

STRONTIUM, BARIUM, AND BERYLLIUM

526. General.—Allied to calcium are two metals of higher combining weight which are very similar to calcium in many respects, and which bear the same relation to it as rubidium and cæsium do to potassium. This relation finds expression not only in similar differences of the combining weights, but also in isomorphism, in the relative frequency of occurrence on the earth's surface, and in many other respects. The general summary of these points of agreement will be given at the end of the book.

These two metals are called *Strontium* and *Barium*. They are, it is true, much rarer than calcium, but cannot be designated as rare elements in the same sense as rubidium and cæsium can. On the contrary, they are of sufficiently frequent occurrence to allow of their being characterised as elements as early as the eighteenth century (strontium in 1792 by Hope, barium in 1774 by Scheele), and of their compounds being applied for various purposes.

527. Strontium has the combining weight 87·6, and occurs in nature chiefly as *sulphate* and *carbonate*. Metallic strontium can be fairly readily obtained by the electrolysis of the fused chloride ; it can also be obtained by preparing strontium amalgam by the action of sodium amalgam on a concentrated solution of strontium chloride, and distilling off the mercury. It is a yellowish, rather tough metal which energetically reacts with water even at room temperature.

Strontium forms only the *divalent ion* Sr$^{\cdot\cdot}$, whose solutions are colourless, and whose heat of formation is 501 k_j.

528. Strontium Oxide, SrO, is obtained by heating the carbonate or, more easily, the nitrate. The dissociation of strontium carbonate takes place with much greater difficulty than in the case of calcium carbonate, i.e. at the same temperature its dissociation pressure is considerably smaller (p. 521). Strontium oxide unites with water to form *strontium hydroxide* with great evolution of heat. The latter can also be obtained directly from the carbonate by heating this in a current of steam ; the decomposition then occurs more easily.

without this aid   This is due, on the one hand, to the fact that the partial pressure of the carbon dioxide is diminished by the steam (p 522), and, on the other hand, to the fact that in place of the oxide there is formed the hydroxide, which stands on a lower level.

529 Strontium Hydroxide is more readily soluble in water than calcium hydroxide. From the hot saturated solution there are deposited, on cooling, hydrated crystals of the composition $Sr(OH)_2$. $8H_2O$ The solution exhibits the properties of a strong base, and the determination of the electrical conductivity shows that there is a large degree of dissociation into the ions $Sr^{..}$ and $2OH'$.

530 Strontium Carbonate occurs as a mineral under the name *strontianite*. This crystallises in forms of the rhombic system, which are isomorphous with those of aragonite (p. 520) ; a form corresponding to calc spar is not known. When the ions $Sr^{..}$ and CO_3'' come together in aqueous solution, strontium carbonate is deposited as a white, very difficultly soluble precipitate, which soon passes into the crystalline state.

Strontianite is used as the initial substance in the preparation of other strontium compounds. Other salts can be readily obtained from it, as the carbonic acid can be expelled by almost all acids. In order to convert strontianite into strontium hydroxide (an operation which is of importance on account of the use of the latter in the sugar industry), it can be heated in steam. It is also converted into strontium oxide when heated with charcoal: $SrCO_3 + C = SrO + 2CO$. This reaction is facilitated by water vapour : $SrCO_3 + C + H_2O = Sr(OH)_2 + 2CO$ (*vide supra*).

531 Strontium Sulphate, $SrSO_4$, is a white salt which is very difficultly soluble in water , it occurs naturally as *celestine* (so-called from its frequently being of a blue colour, due to impurities). The mineral crystallises in rhombic forms, and is isomorphous with anhydrite.   From aqueous solution it is obtained as a white precipitate when the ions $Sr^{..}$ and SO_4'' come together   Its solubility places it at the limit of what can be used in analysis ; when necessary, therefore, the solubility is reduced by the addition of alcohol.

In order to convert strontium sulphate into other salts, it is reduced to strontium sulphide with charcoal: $SrSO_4 + 4C = SrS + 4CO$. this can be easily decomposed with acids. To prepare the hydroxide from it, the sulphide is heated in a current of steam : $SrS + 2H_2O = Sr(OH)_2 + H_2S$.   By systematic crystallisation from aqueous solution, also, the sulphide can be decomposed, as in the case of calcium (p. 530), into hydroxide, which crystallises out, and hydrosulphide which remains in solution ; by boiling the solution sulphuretted hydrogen can be expelled and the separation can thus be effected

532 Strontium Nitrate, $Sr(NO_3)_2$, crystallises anhydrous, and readily soluble in water ; it is used in pyrotechnics for making red

fire   For this purpose it is mixed with potassium chlorate and a combustible substance, sulphur or charcoal.   Strontium has the property of imparting a red colour to flames, and by this means it can be readily detected, as the coloration also appears in the non luminous gas flame.   The spectroscopic decomposition of this dazzling light shows it to be fairly complex ; a sharp blue line is the most characteristic.

533   **Barium**, Ba, has the combining weight 137·4, and occurs naturally as sulphate and carbonate.

Metallic barium is of a white colour, melts at a red heat, and reacts more energetically with water than strontium or calcium.   We have here, therefore, a repetition of the same state of affairs as in the group of alkali metals, viz. the action with oxygen and oxygen compounds is more energetic the higher the combining weight of the metal.

Metallic barium is prepared by the same methods as were given for strontium.   It has as yet not found any application whatever.

Barium forms only the divalent ion $Ba^{..}$, which is colourless and has a poisonous action on the organism.   It can be readily detected by means of the exceedingly difficultly soluble precipitate which it yields with sulphanion, SO_4''.

534. **Barium Oxide**, BaO, is obtained most readily as a white, heavy, crystalline mass, by the decomposition of the nitrate by heat, nitrogen peroxide and oxygen being evolved and barium oxide remaining behind : $2Ba(NO_3)_2 \cdot 2BaO + 4NO_2 + O_2$.   The temperature at which barium carbonate loses its carbon dioxide is so high that it is not suitable for the preparation of the oxide.

The oxide unites with water, with the evolution of much heat to form *barium hydroxide* or *baryta*, $Ba(OH)_2$.   This is still more readily soluble in water than strontium hydroxide and, like the latter, it crystallises from its hot saturated solutions in large crystals with $8H_2O$.   A solution saturated at room temperature contains 3·7 per cent hydroxide ; it is therefore about ¼th normal (p. 191) with respect to hydroxyl.

Baryta is used for various purposes.   Its dilute solution is used for the volumetric estimation of acids (p. 189) ; for this purpose it is specially suitable from the fact that it attacks glass much less than a corresponding solution of caustic potash or soda, and because it can never contain carbonate, from the fact that barium carbonate is a very difficultly soluble salt, and is therefore precipitated as soon as it forms.   This last circumstance is of importance, because the presence of carbonic acid renders the reactions of alkalimetric indicators indistinct, and therefore impairs the exactness of the determination.   To prevent the atmospheric carbon dioxide changing the titre of the solution, the bottle and burette used for baryta are furnished with guard tubes filled with soda lime, and are always kept connected with one another, as is shown in Fig. 115.   The burette is filled by sucking at the india-rubber tube *g* and opening the clip *h*.

Baryta is also used in analytical chemistry in cases where it is [nec]essary to employ a strong base, the excess of which can be subse[quent]ly readily removed. Thus magnesium is separated from potas[sium] and sodium by preparing the [chlorid]es and adding excess of baryta [to a] solution of these. All three [metal]s are thereby converted into [hydrox]ides, that of magnesium is [precipit]ated, while those of the other [two,] along with the excess of [baryta,] remains in solution. If carbon [dioxid]e is now passed into the solu[tion, t]he barium is precipitated as [carbon]ate, and, after filtration, there [is obta]ined a solution of the alkali [hydrox]ides. The precipitate consists [of bar]ium sulphate, barium carbonate, [and m]agnesium hydroxide; it is [treate]d with dilute sulphuric acid, [wherel]by the magnesium hydroxide [passes] into solution as sulphate, and [the] barium is converted into [sulpha]te. The two can be easily [separa]ted by filtration.

[For] manufacturing purposes also, [baryta] can be similarly employed. It has already been mentioned that [the ca]ustic potash or caustic soda can be prepared from the sulphates [by mea]ns of baryta (p. 483).

Fig. 115.

[For] the preparation of baryta, barium sulphate is chiefly employed. [It is] reduced to sulphide by means of charcoal, and converted into [the ox]ide with steam (cf. the corresponding processes in the case of [calci]um). From the solution of the sulphide, also, the sulphur can [be rem]oved by boiling with a metallic oxide, e.g. copper oxide. $BaS + H_2O = Ba(OH)_2 + CuS$.

[53]5. Barium Sulphate, $BaSO_4$, occurs fairly widely distributed [in natu]re as the mineral heavy spar or barytes. Both these names are [in allus]ion to the great density which this compound, like all barium [compoun]ds, exhibits; it amounts to 4.5, while that of most of the non[metalli]c minerals is about 2.5.

[Ba]rium sulphate crystallises in rhombic forms, and is isomorphous [with an]hydrite and celestine. It is formed in all cases where the ions [Ba and] SO_4 come together, and, as it is very difficultly soluble, it is [immed]iately deposited as a white, heavy precipitate. The use of [soluble] barium salts, i.e. of barium, for the detection and determination [of sulp]hanion, which follows from the above reaction, has already been [severa]l times mentioned.
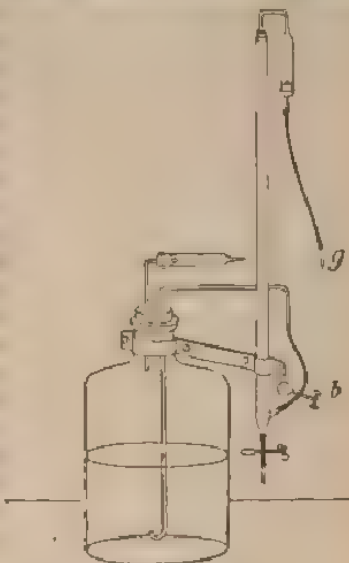
Since sulphuric acid is a strong acid, other acids do not have as great solvent action on barium sulphate. Further, since barium can in no way pass into other more complex ions, there is no solvent whereby barium sulphate can be rendered soluble in aqueous liquids. It can be dissolved only in some substances which do not have an ionising action, e.g. concentrated sulphuric acid. So soon, however, as the ions are caused to be formed by dilution with water, the barium sulphate is again precipitated.

On account of this resistance to chemical attack, the naturally occurring heavy spar, when cut in plates, is used in the manufacture for lining apparatus in which strong acids are worked with. The artificially prepared barium sulphate is used as a pigment, under the name *permanent white*. It is prepared by dissolving the naturally occurring barium carbonate in hydrochloric acid, and precipitating the clarified liquid with sulphuric acid. Hydrochloric acid is regenerated and can be used for dissolving further quantities of carbonate.

In order to convert barium sulphate into other barium compounds, it is reduced with charcoal to *barium sulphide*, which can be readily decomposed by acids with evolution of sulphuretted hydrogen. By fusion with excess of alkali carbonate it is converted into *barium carbonate*; the alkali sulphate which is formed can be removed by washing.

536. Barium Carbonate, $BaCO_3$, occurs naturally, as *witherite*, in rhombic crystals which are isomorphous with aragonite and strontianite. It is used as a convenient starting material for the manufacture of other barium salts, for which purpose the substance is decomposed by acids. Its conversion into oxide by heating is not practicable, because the temperature of measurable dissociation is too high.

On bringing the ions Ba'' and CO_3'' together, barium carbonate is obtained as a white precipitate, readily soluble in almost all acids.

In preparative chemistry, pure barium carbonate is very largely used for the preparation of the barium salts of the most varied acids. These mostly crystallise well, and can therefore be easily freed from impurities. Their most important property is, however, that they are suited for the preparation of the free acid in aqueous solution, because they are all decomposed by sulphuric acid, barium sulphate being thereby precipitated, and the acid in question remaining free in solution. Examples of this have already been given (e.g. p. 215).

537. Barium Chloride, $BaCl_2$, is obtained by dissolving witherite or barium sulphide (from sulphate and charcoal) in hydrochloric acid; on concentrating the solutions, barium chloride crystallises out in lustrous, heavy crystals with $2H_2O$, which become anhydrous only at a fairly high temperature. Unlike the chlorine compounds of the other metals of this group, barium chloride does not lose hydrochloric acid on dehydration, but maintains its neutral reaction.

Barium chloride is used in the laboratory as a reagent for the detection and estimation of sulphanion.

538   Barium Nitrate, $Ba(NO_3)_2$, is a salt which is not abundantly soluble in water, and which is employed in analytical chemistry in place of barium chloride, when it is not desired to introduce chloridion into the solution.   If free nitric acid is added to a saturated solution of the salt, a crystalline precipitate of barium nitrate is soon deposited. The same occurs when nitric acid is added to the solution of any other barium salt.

This reaction is not especially peculiar to barium nitrate, but depends on the increase of the nitranion by means of nitric acid and the corresponding overstepping of the solubility product (p. 447), in the case of barium nitrate, however, the phenomenon is specially well marked, because this salt stands at the limit of those which are designated as soluble (100 parts of water dissolve about 9 parts of the salt at 18°), and its solubility product is therefore easily exceeded. The beginner is sometimes deceived by this precipitate, mistaking it for barium sulphate; the distinctly crystalline nature and the solubility in pure water, after pouring off the mother liquor, are, however, sufficient to distinguish them.

Barium nitrate is used in pyrotechnics for the preparation of green fire.   The green flame-coloration is produced also in a non-luminous gas flame, especially when the specimen containing barium is moistened with hydrochloric acid.   On spectroscopic examination it yields a fairly complicated spectrum, which is characterised by a sharp yellow-green and a sharp, although less bright, green-blue line, along with several broad bands.

539   Barium Peroxide, BaO_2, is obtained as a white powder by heating barium oxide to a temperature between 450° and 550° in a current of oxygen.   At a higher temperature it again loses oxygen, and the equilibrium between the solid oxide and peroxide and the gaseous oxygen, is governed by exactly the same laws as the dissociation of calcium carbonate (p. 521).

Barium peroxide is important as being the most convenient starting substance for the preparation of hydrogen peroxide (p. 156).   For this purpose it is treated with dilute acid, whereby the reaction occurs : $BaO_2 + 2H = Ba^{..} + H_2O_2$.   The anion of the acid forms the corresponding barium salt, e.g. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.

* It would apparently be most suitable to carry out this reaction with sulphuric acid, because the barium sulphate, being practically insoluble, would be deposited and leave a pure solution of hydrogen peroxide.   This, however, cannot be done, since sulphuric acid scarcely attacks the anhydrous barium peroxide.   The reaction, however, readily occurs with hydrochloric acid, and the operation is carried out as follows.   A certain amount of hydrochloric acid is saturated with peroxide, the barion is precipitated with sulphuric acid, and the solu-

tion, which now contains hydrochloric acid, is allowed to act on fresh portions of peroxide. These alternate operations are continued until sufficient hydrogen peroxide has accumulated in the solution. The chloridion is then precipitated by the addition of silver sulphate, and the sulphanion thereby introduced is removed with baryta.

Another method is to first add a small quantity of baryta water to the hydrochloric acid solution of peroxide in order to remove the metallic oxides present as impurities, and then to precipitate the filtered liquid with baryta. Barium peroxide again separates out now, however, in the form of a crystalline hydrate, which can be readily decomposed with sulphuric acid. The hydrate is freed from the barium chloride present by washing, and is preserved for use in the moist state, since on being dried it again becomes more difficultly decomposable. The composition of the hydrate is $BaO_2 . 8H_2O$.

540. **Beryllium**. Beryllium occupies the same position among the alkaline earth metals as lithium does among the alkali metals. Its combining weight is the smallest, and its similarity to the other elements of the group is least. Its properties exhibit a distinct tendency towards the next group, that of the earth metals. The combining weight of beryllium amounts to 9·1.

Metallic beryllium can be prepared by electrolysis, by the reduction of the oxide with magnesium, of the chloride with sodium, and in other ways. It is a white metal, which is still more stable to moist air than magnesium, and decomposes water only slowly even when heated. It is readily dissolved by dilute acids, with evolution of hydrogen, and passes thereby into the ionic state.

Besides the typical divalent ion Be¨, beryllium also forms other ions containing oxygen; these will be discussed later. Of the metals hitherto considered, it is the first that is capable of forming different ions.

Beryllion, Be¨, is colourless and is distinguished by a conspicuously sweet taste. This fact procured for the element the passing name of *glucinum* (still occasionally used in France and England); the name beryllium is derived from that of its most important naturally occurring compound, *beryl*, which is a silicate containing aluminium.

Beryllion forms various salts, of which the chloride, $BeCl_2$, and the sulphate, $BeSO_4$, are the best known. They are both soluble in water, and the solutions react acid. This is due to incipient hydrolysis, since beryllium hydroxide is a weak base.

Beryllium hydroxide, $Be(OH)_2$, is obtained as a white, gelatinous precipitate on bringing beryllion and hydroxidion together; it is not measurably soluble in water, and has no basic reaction. It dissolves in acids, with formation of beryllium salts, and on being heated is converted into a white powder of beryllium oxide.

Beryllium hydroxide dissolves in caustic potash or caustic soda. Since these bases, by reason of their containing hydroxyl, should, in accordance with well-known principles, *diminish* the solubility of beryl-

hydroxide, this contradiction requires an explanation. This is met by the fact that the compound BeO_2H_2 can split off hydrion and behave like a very weak acid. Accordingly, it gives the two ions O_2 and BeO_2' (just as carbonic acid gives the ions HCO_3' and), and it is these and not beryllion, Be'', that are present in the solution in question. The compound is also obtained by fusing beryllium hydroxide with caustic soda and dissolving the melt in water. If this alkaline solution is allowed to stand a long time, or if it is heated to boiling, almost all the beryllium hydroxide is precipitated. The question now arises why the chemical equilibrium, which had previously existed, is now disturbed, since no new substance has been added. The answer is to the effect that the beryllium hydroxide which is precipitated is a different, and indeed a more stable and less soluble, form of the hydroxide than the freshly precipitated form which is soluble in alkalis. In other words, the newly prepared solution is *supersaturated* with respect to the *more stable form* of the hydroxide, and therefore cannot continue to exist when the latter form is present. Since this form is not present in the newly prepared solution, the precipitation can commence only after the first traces of it have been formed. At the ordinary temperature this occurs slowly, more quickly when heated.

541. Summary.—The properties of the corresponding compounds of the elements of the second group change in the same order as the combining weights, so that the relations which here prevail can be easily impressed on the memory by making the sense clear in which the change takes place. In the following table the properties which have been considered are given, and the arrows which are added indicate whether the values of these increase ($\rightarrow$) or decrease ($\leftarrow$) with increasing combining weight.

PROPERTIES OF THE ALKALINE EARTH METALS AND OF THEIR COMPOUNDS

Combining weight	$\rightarrow$
Reactivity of the metal	$\rightarrow$
Basicity of the elements and of the corresponding compounds	$\rightarrow$
Basic properties of the hydroxides . .	$\rightarrow$
Solubility of the hydroxides	$\rightarrow$
Solubility of the halogen compounds, nitrates, and sulphates	$\leftarrow$

CHAPTER XXVI

ALUMINIUM AND THE OTHER EARTH METALS

542 General.—The group of the earth metals, to which we now turn, is characterised by the fact that the elements contained in it form *trivalent cations*. The parallelism which exists between the elements of the first and second groups in respect of combining weights and general character, is also found here, with, however, an essential difference. Of the elements of the third group, there is *one* which occurs frequently in the earth's crust; but this one is found in great abundance. All the other elements are exceedingly rare, and their properties and compounds are therefore comparatively little known.

The diminution of the reactivity of the metal with oxygen and water, which was met with in some of the members of the second group, is found here in a still higher degree, so that *aluminium*, the most important element of the third group, is a metal which is at the present day applied in the arts, and as such plays a not inconsiderable rôle. At the same time, the basic properties of the hydroxides, a weakening of which was also indicated in the second group, have become so small that there is no strong base in this group. As usual, it is in the case of the elements with *small* combining weight that this effect is most conspicuous; in the case of the first element which must be included in this group, viz. *boron*, the complete reversal has already taken place, for this element has entirely lost its metallic character, and forms an acid hydroxide, boric acid (p. 435).

The elements belonging to this group, together with their combining weights, are :—

Boron (11·0), aluminium (27·1), scandium (44·1), yttrium (89·0), lanthanum (138·9), etc., ytterbium (173). With regard to these we would make the following remarks.

While the combining weights from boron to lanthanum correspond to those of the metals lithium to cæsium and beryllium to barium, we have here a higher member, ytterbium, with a combining weight of 173, which is not represented in the first two groups. It may be

presumed that such representatives do exist, but have not yet been discovered.

Further, an etc. has been inserted after lanthanum. This signifies that there exist at this point not *one* element but a number of elements which are all very close to one another, and have therefore an almost equal claim to this position. This occurrence of several elements with small differences recalls the occurrence of numerous small planetary bodies at a part of the solar system where, by analogy, one would have expected a large planet.

543 **Aluminium.** — Of all the light metals, aluminium is the most widely distributed on the earth's surface. It forms a constituent of almost all *crystalline silicate rocks*, and of the secondary formations, the *clays* and *slate* formations are formed from aluminium silicate. A knowledge of the compounds of this metal, therefore, extends back as far as chemical knowledge at all can be traced.

From the time of the discovery of the alkali metals, it was regarded as indubitable that a *metal* must be contained in clay. Wöhler, however, was the first to obtain metallic aluminium by the action of sodium on the chloride. The method of separating the element from its compounds by *electrolysis* was given by Bunsen (1854).

The name aluminium is derived from *alum* (*alumen*), because aluminium is contained in this long-known salt.

At the present day, aluminium is prepared on a very large scale by the electrolysis of its oxide. The oxide is fused by the heat developed by the passage of the electric current, the aluminium goes to the cathode, and the oxygen which separates at the anode combines with the charcoal, of which the anode consists, to form carbon monoxide. To facilitate the fusion, the electrolytic vessel also contains other compounds of aluminium, *e.g.* cryolite (*vide infra*); since oxygen is more readily separated than fluorine (which is the corresponding other constituent of cryolite), this addition does not alter the chemical action, and only aluminium oxide requires to be thrown in to replace the used up material.

Metallic aluminium is a white, somewhat bluish metal which remains tolerably unchanged in the air. This is due to the fact that it speedily becomes covered with an invisible, thin, and firmly adhering layer of aluminium oxide, which protects the metal underneath like a varnish. It melts at 700°, and can be both cast and mechanically wrought into the shape desired, as it is not hard and is very ductile. Thus thin wire and very thin foil, like gold-leaf and silver-leaf, can be made; the latter is greatly used for "silvering," since sulphurous gases do not blacken it. Aluminium is a good conductor for heat and electricity.

On account of its lightness (density = 2·7), its silver-like lustre, and its durability in the air, aluminium, especially since the electrolytic method has rendered it cheap, has become greatly used for ordinary

utensils, but it does not seem hitherto to have been received with
entire favour. This is perhaps to be accounted for by the fact that
although it resists the action of pure water, it is rather strongly
attacked by salt solutions of all kinds. Further, the oxidation of the
metal generally occurs in spots, so that holes are there formed which
can be repaired only with difficulty. Its resistance to mechanical
action also is small.

* When aluminium is alloyed with *mercury*, it appears to assume
quite different properties. It is amalgamated by rubbing its surface
with a mercury salt, *e.g.* mercuric chloride, with some pressure. The
parts which were at first bright on account of the mercury, immedi-
ately become dull, and a moss like growth of aluminium hydroxide
arises from them. This phenomenon is explained by the fact that
although the protecting layer of oxide is formed at the amalgamated
parts, the coating does not adhere, on account of the liquid nature of
these, and the oxidation, therefore, pursues its course. It is not that
the mercury produces an increased reactivity of the aluminium (a
thing which is theoretically impossible), but the real chemical activity
of the aluminium is allowed free scope to exert itself

* The amalgamated aluminium is employed as a reducing agent.
On account of this behaviour, objects made of aluminium must be
carefully protected from contact with mercury.

While, even at comparatively high temperatures, massive aluminium
is only superficially and inappreciably attacked by oxygen, the finely
divided metal burns with a brilliant light at a red heat. This can be
shown by holding aluminium foil in the flame, or by blowing the
divided metal, such as is used in the form of aluminium bronze,
through the flame. It takes fire, however, with greater difficulty than
magnesium.

Aluminium dissolves in dilute hydrochloric and sulphuric acids
with energetic evolution of hydrogen. In nitric acid it readily
becomes passive, *i.e.* becomes coated with a layer which is not attacked
by the acid, and then remains unchanged. Further, aluminium readily
dissolves in a solution of caustic potash or soda, with evolution of
hydrogen. This is due to the formation from the aluminium of an
anion containing oxygen; we shall return to this later (*vide infra*).
Salt solutions, also, especially solutions of ammonium salts, dissolve
the metal fairly readily.

Aluminium forms alloys with various metals, and some of these are
technically valuable. They will be mentioned under the respective
metals. We would only mention here that an alloy (magnalium) has
been prepared from aluminium and magnesium, which is stated to
have technically valuable properties, and to be stable in the air.

344 **Aluminion**. Aluminium forms a single, elementary, trivalent
ion, Al··· ; it can further act as a constituent of complex ions.

Aluminion is colourless, and its salts are for the most part soluble.

...ave an astringent taste, but have otherwise no great physio
...action. Since aluminium hydroxide is a weak base, all the
...of aluminium are *hydrolytically dissociated* to an appreciable
...in aqueous solution, and therefore react acid. In the case of
...lts of the strong acids, this hydrolysis is slight; in the case of
...lts of weak acids, however, it becomes considerable, especially
...ating.

...like the ions of the other more frequently occurring light
..., aluminion does not occur in measurable amount in natural
... It is separated out from the rocks in the form of *aluminium*
... or *aluminium hydroxide*, an exceedingly difficultly soluble com-
...which, therefore, does not pass into solution.

Aluminium Hydroxide. *Aluminium hydroxide*, Al(OH)$_3$,
...ipitated as a gelatinous, uncoloured precipitate from solutions
...ammonium salts, by the addition of a soluble base; in the air it
...water, and when heated to redness is converted into aluminium
..., according to the equation 2Al(OH)$_3$ = Al$_2$O$_3$ · 3H$_2$O.

...luminium hydroxide is practically insoluble in water, and is a
...weak base. Since it contains three hydroxyls, it can form three
...of salts, in which one, two, or three hydroxyls are replaced by
... Salts in which unreplaced hydroxyl is still present are called
...salts, corresponding to the acid salts which contain unreplaced
...hydrogen. In general, however, the basic salts are much less
...ively characterised than the acid ones; whereas the latter mostly
...lise well, and can therefore be easily prepared in the pure state,
...morphous form predominates in the case of the basic salts, whose
...aration in the pure state is therefore difficult. For this reason
...will, in the sequel, generally not receive special description.

...account of the slight development of basic properties in the
...of aluminium hydroxide, and its exceedingly small solubility, it
...ecipitated even by very weak soluble bases, e.g. by ammonia,
...in presence of ammonium salts. In this way it differs from
...hydroxides of the alkaline earth metals, and can, therefore, be
...for the separation of aluminium from these, especially from
...esium.

...stic potash or soda of course also precipitate aluminium hydrox-
...from the solutions of its salts. The hydroxide, however, readily
...ves in an excess of these substances, and forms clear solutions
...strongly alkaline reaction. This is due to the fact that aluminium
...oxide can also act as an acid by splitting off hydrion from its
...oxyl groups (*vide infra*).

...is property of aluminium hydroxide of acting as an acid, is the
...that metallic aluminium readily dissolves in caustic potash or
...with evolution of hydrogen (p. 558). If such a solution and
...one of aluminium in hydrochloric acid are prepared, and the
...olutions are mixed, aluminium hydroxide is precipitated, and

sodium chloride remains in solution. The reaction is represented by the equation $Na_3AlO_3 + AlCl_3 + 3H_2O = 3NaCl + 2Al(OH)_3$. Taking the reacting ions into account, we should write, $AlO_3''' + Al''' + 3H_2O = 2Al(OH)_3$.

By loss of water, aluminium hydroxide can give rise to various anhydrides, which bear the same relation to one another as the anhydrides of phosphoric acid. According as one, two, or three combining weights of water are eliminated from two combining weights of the hydroxide, there are obtained, besides $Al(OH)_3$, the compounds $Al_2O_3H_4$, AlO_2H, and Al_2O_3.

All these compounds occur in nature : the normal hydroxide $Al(OH)_3$ is *hydrargillite*, $Al_2O_3H_4$ (generally greatly contaminated with other substances) is *bauxite*, AlO_2H is *diaspore*, and Al_2O_3 is *corundum*.

Bauxite is of importance as being the starting substance in the manufacture of metallic aluminium (p. 557). *Corundum* is, on account of its hardness, which is nearly equal to that of diamond, an important mineral technically. It crystallises in rhombohedra. In its fine-grained varieties, called *emery*, it is employed as a grinding material for glass, steel, and other hard substances. Transparent corundum, coloured blue by admixtures, is valued as a gem under the name *sapphire*; a red form, whose colour is due to a small amount of chromium, is called *ruby*, and is also a valuable gem. Small and less finely coloured rubies are used as axle-bearings in watches and other measuring instruments, where movement with as little friction as possible is required. Corundum, in all its forms, is very little susceptible to chemical influences, and it is only with difficulty that it can be converted into soluble compounds by fusion with caustic alkalis or acid sulphates.

546. Aluminates.—The compounds in which aluminium hydroxide occurs as an *acid*, are called *aluminates*. Since aluminium hydroxide contains three combining weights of hydrogen, it must be regarded as a tribasic acid ; since, however, it is a very weak acid, the normal compounds, in which all three hydrogens are replaced, are not easy to prepare, and in aqueous solution they decompose to a greater or less extent owing to hydrolysis.

A substance which is capable of acting at the same time as acid and as base, can be only a *weak* acid and base. For the acid action necessitates the presence of hydrion ; the basic action, that of hydroxidion. The two kinds of ion, however, cannot be present *together* in any great concentration, since they would unite to form water, which is only very slightly dissociated. If, therefore, an acid is strong, *i.e.* splits off much hydrion, it certainly cannot split off more than an exceedingly small amount of hydroxidion, the amount of which is limited by the chemical equilibrium of the two ions in water. The same holds for weak bases.

As in the case of phosphoric acid, the aqueous solutions of the aluminates contain three different anions, viz. the monovalent H_2AlO_3', the divalent $HAlO_3''$, and the trivalent AlO_3'''. Since we are dealing with a weak acid, the monovalent ion will predominate.

Of the aluminates, the *sodium compounds*, more especially, are known: they correspond to the three possible types, NaH_2AlO_3, Na_2HAlO_3, and Na_3AlO_3. These substances are soluble in water, and do not crystallise well; their solutions react strongly alkaline, and are very unstable. For if such solutions, especially of the first and second types, be kept some time, they lose a great part of the alumina they contain, this being deposited as a crystalline precipitate on the bottom of the vessel. This is due to the same phenomenon as in the case of iron hydroxide (p. 554), the aluminium hydroxide which is deposited is a *more stable* form than the *amorphous* and gelatinous one, and solutions, therefore, which are saturated with respect of the latter are supersaturated with respect of the former. Accordingly, so soon as the first crystals of the more stable form are produced, it continues to separate out, and does not stop until the new equilibrium is reached.

Aluminium hydroxide is not appreciably soluble in *ammonia*, because the basic properties of the latter are too weak. That is to say, if ammonium and aluminanion are brought together, they pass into the undissociated compounds, ammonia and aluminium hydroxide, as is shown by the equation $H_2AlO_3' + NH_4' = Al(OH)_3 + NH_3$. This behaviour is made use of in analysis. When it is required to precipitate aluminium hydroxide from an aluminate, an acid may be used for the purpose; an excess of the acid, however, again dissolves the alumina, and it is therefore difficult to effect a complete separation. If, however, an ammonium salt be added to the solution of an aluminate, the above reaction takes place and the alumina is deposited, while an excess of ammonium salt exerts no solvent action.

The other light metals also form aluminates. Of these, the naturally occurring *spinel* is of interest: this can be regarded as the aluminate of monomagnesium aluminate, $MgH_4Al_2O_6$, for it has the composition $MgAl_2O_4$, and $MgH_4Al_2O_6 - 2H_2O = MgAl_2O_4$.

Spinel crystallises in the regular system, generally in rhombic dodecahedra, and is the type of a fairly large series of corresponding isomorphous compounds which are composed of equal combining weights of the oxides of a divalent and a trivalent metal, for the formula of spinel can also be written MgO, Al_2O_3.

Since the place of magnesium can be taken by iron, manganese, zinc, etc., and that of aluminium by chromium, iron, manganese, etc., there are a large number of compounds of the type of spinel, some of which will be mentioned later. They all crystallise in the regular system.

547 Aluminium Chloride. The compound $AlCl_3$ is formed

2 o

when metallic aluminium is heated in a current of hydrogen chloride. Hydrogen is liberated, and aluminium chloride readily sublimes, forming a white crystalline mass in the colder parts of the apparatus. Formerly, when aluminium was not a cheap substance, the salt was prepared by heating a mixture of aluminium oxide and charcoal in a current of chlorine. The process is represented by the equation:

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$$

Aluminium chloride boils at about 183°. The melting point is somewhat higher—193°; on being heated, therefore, under ordinary pressure, it passes directly from the solid into the vaporous state. By heating it in a closed vessel, so that the boiling point is raised, it can be fused.

* Aluminium chloride is used in organic chemistry in numerous preparations, which depend on the fact that in presence of aluminium chloride, mixtures of a chlorine and a hydrogen compound split off hydrogen chloride, the residues then combining to form the new compound. In organic chemistry such a process is called *synthesis* (in the narrower sense), and for such purposes aluminium chloride is of especial importance.

Aluminium chloride fumes in the air and reacts with water with a very considerable evolution of heat. Anhydrous aluminium chloride cannot be again obtained from the aqueous solution; from the strongly concentrated solution a salt crystallises out with $2H_2O$, which, on being heated, completely decomposes into hydrogen chloride which escapes, and aluminium oxide which remains behind: $2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl$.

Aluminium chloride readily unites with other chlorides to form double salts, and more especially so with *potassium* and *sodium chlorides*. These compounds crystallise well, and in them aluminium chloride has lost its volatility. The sodium compound melts with exceeding ease, and was formerly used as the starting substance for the preparation of metallic aluminium.

On account of its ready volatility, the molar weight of aluminium chloride was early determined, and was found, in agreement with certain theoretical assumptions, to correspond to the formula Al_2Cl_6. Subsequently, these theoretical views became doubtful, and a thorough investigation showed that in the neighbourhood of the boiling point, certainly, vapour densities were observed which corresponded approximately to this formula (although they were always too low), but that the values rapidly diminished as the temperature rose, and at temperatures between 450° and 760° remained constant and corresponded to the formula $AlCl_3$.

548. Aluminium Bromide and Aluminium Iodide are very similar to the chloride, but less volatile. They are readily formed from the elements, and in organic chemistry have a use similar to that of the chloride.

Aluminium Fluoride, AlF_3, is obtained at a red heat from aluminium and hydrogen fluoride, and also from aluminium oxide and hydrogen fluoride, and is very much less volatile than the other compounds of aluminium. It forms small, lustrous crystals which behave indifferently towards water, and scarcely dissolve in it. If alumina is treated with aqueous hydrofluoric acid, it dissolves in quantity. The solution, however, is strongly supersaturated with respect to the above difficultly soluble form of aluminium fluoride, which is slowly deposited spontaneously.

Aluminium fluoride is soluble in hydrofluoric acid, and forms with it a *hydrofluoaluminic acid*, H_3AlF_6, the *sodium salt* of which is very difficultly soluble in water. It occurs in large quantities in Greenland, and as a mineral this compound, Na_3AlF_6, is called *cryolite*.

Cryolite is used for the preparation of *soda* along with *pure aluminium hydroxide*. For this purpose it is heated with milk of lime, or fused with lime, whereby calcium fluoride and sodium aluminate are formed; the latter passes into solution or can be extracted with water. $Na_3AlF_6 + 3CaO = 3CaF_2 + Na_3AlO_3$. The latter solution is decomposed by passing in a current of carbon dioxide, whereby sodium carbonate is formed and aluminium hydroxide is precipitated. $2Na_3AlO_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2Al(OH)_3$.

Aluminium Sulphate. Of all the salts of aluminium, the sulphate is the one which has the largest application, and it is therefore manufactured on a large scale. It is obtained by heating aluminium hydroxide with sulphuric acid: the solution produced solidifies, at a suitable concentration, to an indistinctly crystalline mass of the formula $Al_2(SO_4)_3 \cdot 18H_2O$. The sulphate can also be prepared by heating aluminium silicate with sulphuric acid, silicic acid being thereby set free. A pure salt can be obtained from the commercial product by precipitating the concentrated solution with alcohol. An oily liquid is then deposited, which is a supersaturated solution of aluminium sulphate in water (with a very little alcohol), which soon solidifies to lustrous scales of a salt with $18H_2O$.

It is no rare thing for aqueous solutions of salts which are readily soluble in alcohol, to be first precipitated, by the addition of the latter, as a concentrated solution which is immiscible with the rest of the alcoholic solution. The formation of the supersaturated solution before that of the solid crystals is only another case of the *occurrence of the less stable forms*.

On account of hydrolysis, the aqueous solution of aluminium sulphate reacts acid. It can dissolve fairly considerable quantities of aluminium hydroxide, with formation of basic salts; difficultly soluble salts are ultimately deposited.

A basic aluminium sulphate, in which only one of the three equivalents is replaced by sulphanion, $Al_2(OH)_4SO_4 \cdot 7H_2O$, occurs

naturally as *aluminite*, and is used in the preparation of the normal aluminium sulphate, and of its double salt, *alum*.

551. **Alum** was the name given originally to a double salt of aluminium and potassium sulphate, $AlK(SO_4)_2 . 12H_2O$, which crystallises in fine octahedra belonging to the regular system, on mixing the solutions of the single salts. In the cold it is much less soluble than the single salts, and a solution prepared from the saturated solution of these is strongly supersaturated in respect of alum. The supersaturation does not, it is true, disappear spontaneously, as the solution is in the metastable condition; in our surroundings, however, so alum is so largely distributed that scarcely an object which has been in the air is free from it. As a rule, therefore, the nucleus which is necessary for the formation of crystals is immediately present; if this is excluded by heating the liquids and vessels to 100 (whereby the alum melts in its water of crystallisation) and the entrance of dust avoided, crystallisation remains suspended for any length of time.

Alum was formerly the most important *salt of aluminium*. Although the potassium sulphate contained in it had either no effect or had a disturbing effect in its applications, alum was nevertheless employed, because none of the simple salts of aluminium crystallise well, and thus cannot be easily freed from impurities. Since the method was discovered of preparing pure aluminium hydroxide by way of sodium aluminate), and so of preparing pure aluminium sulphate from this, alum has lost its importance, and is now being more and more replaced by the simple sulphate.

With this also, the former methods of preparing alum are beginning to disappear. It used to be prepared from a basic potassium aluminium sulphate, which occurs naturally as *alum-stone*, by heating this and extracting with water; alum thereby passed into solution and aluminium hydroxide remained behind. Further, it was obtained from *alum shale*, a silicate of aluminium permeated with sulphide of iron. This was roasted, and then allowed to undergo oxidation in the air. From the sulphur of the iron sulphide, sulphuric acid is formed; this converts the aluminium silicate into sulphate, which is then extracted with water and made to crystallise by the addition of potassium sulphate.

On being heated, alum melts in its water of crystallisation; on raising the temperature, it loses its water and forms a spongy, white mass called *burnt alum*. The latter is used in medicine.

The most important use of aluminium sulphate, or of alum, is in *dyeing*. Many dyes are incapable of combining directly with the fibre of the cloth in such a way that the colour is not withdrawn by water and soap. If, however, the cloth is previously treated with aluminium salts it can be permanently dyed. This is due to the fact that the fibre absorbs and unites with the aluminium hydroxide, which is always present in the solution, as the aluminium salts are always

somewhat hydrolysed. Further, the dyes have the power of uniting with aluminium hydroxide to form the practically insoluble, finely divided "lakes," and in this way the union between the dye and the fibre is effected by the aluminium hydroxide.

Potassium aluminium sulphate is the type of a large series of other salts, which have a similar composition, and crystallise in the same forms of the regular system. The place of potassium can be taken by *cæsium*, *cæsium*, *ammonium*, and a large number of *organic derivatives of ammonium*, as well as by the heavy metal *thallium*, but not by sodium or lithium. The place of aluminium can be taken by other metals, which form *trivalent* ions, such as *iron*, *chromium*, *manganese*, *indium*, etc. Finally, in place of the sulphanion we can have selenanion, SeO_4''. Hence, we have a great diversity here; for all these double salts the name *alum* has been adopted, the names of the metals present being prefixed. These alums are isomorphous with one another, and the supersaturated solution of one of them is made to crystallise by a nucleus of any other.

552 **Aluminium Silicate.** It has already been several times mentioned that the rocks of which the earth's crust was primarily formed consist essentially of silicates, the metals of which, besides the constant alkali and alkaline earth metals, formerly mentioned, are aluminium and iron. On undergoing decomposition by water and carbon dioxide ("weathering"), the first mentioned pass into carbonates, while magnesium partially, and aluminium entirely, remain behind as simple silicates.[1]

Aluminium silicate is called *clay*, and is formed in the amorphous state, and in very finely divided form, in the weathering of the rocks. As a result, it is readily carried away by flowing water, and is deposited only when the movement of the water becomes very slow. According to the degree of purity, it possesses various properties, and is called by different names.

The purest form is called *kaolin*, or *china clay*, and is generally found in localities where rocks, poor in magnesium, are decomposed by water and carbon dioxide, but are not transported mechanically. The water has then carried away the other constituents in solution, and the aluminium silicate, with more or less quartz, has remained behind.

Less pure forms, which are frequently contaminated, more especially with calcium carbonate, quartz, and iron oxide, are called *clay*, or *potter's earth*. *Marl* contains a large quantity of calcium carbonate, and *loam* contains quartz sand as well.

The use of aluminium silicate is very old, and widely extended. It depends on the fact that it yields a tenacious mass *with water*, capable of being moulded; on drying, this undergoes regular contraction, and

[1] Under certain conditions occurring in the tropics, which, however, cannot as yet be explained in detail, aluminium silicate is also decomposed, in such a way that silicic acid is carried away while aluminium hydroxide (as bauxite) is left behind.

. . . finest materi . . .
. . . m silicate, wi . . .
. . . latter is a dou . . .
. . . moulded and s . . .
. . . "biscuit ware " . . .
. . . spar and water; . . .
. . . red with a thin, re . . .

ed in them   Ordinary felspar, or *orthoclase*, is potassium aluminium
ate, $AlKSi_3O_8$.   It occurs widely distributed in monoclinic crystals,
must be regarded as one of the most important sources of potash
the soil   The *soda felspar* or *albite*, has a corresponding composi
, containing sodium in place of potassium; it is *triclinic*   *Anorthite*
a calcium felspar, which is isomorphous with albite, and can unite
h it in all proportions to form mixed crystals; it has the composi
$Al_2CaSi_2O_8$ Some of these mixtures have received special names,
h as *oligoclase* and *labradorite*

Another group of alkali aluminum silicates is that of *mica*, which
distinguished by its power of cleaving, its elasticity, and resistance
high temperature.   Some kinds of mica contain magnesium in place
the alkali metals.   The formula is doubtful.

554   Other Salts of Aluminium.—Since in using aluminum
phate as a *mordant* in dyeing, the alumina is deposited on the fibre,
a corresponding amount of acid remains in the solution, and as it
creases it begins to hinder the deposition.   By using a weak and
latile acid, the process can be carried on to much greater advantage;
r such purposes, therefore, *aluminium acetate* is used.   This salt is
tained from aluminum sulphate by decomposing it with barium or
ad acetate, whereby the corresponding sulphate, being insoluble, is
posited.   The same object is attained more simply by the addition
any soluble acetate, *e g* sodium acetate, since this has the same
ect in diminishing the concentration of hydrion.

Aluminium acetate is a very decomposable salt, even on boiling
aqueous solution it is decomposed into alumina (or a very basic
ate) which is precipitated, and acetic acid, which remains in solution.
is is due to the increase of hydrolysis with rising temperature.   For,
ce the hydrolysis depends on the amount of hydrion and hydroxidion
tained in the water, and since this increases with rising tempera-
re, because the dissociation of water into its ions is accompanied by
sorption of heat, the degree of hydrolysis must also increase as the
mperature rises.   Moreover, the reaction is thereby accelerated, and
ny persisting supersaturation therefore excluded.

Aluminium Phosphate occurs as a mineral in various forms.   It
best known as *turquoise*, which is used as a gem, and is coloured
ue owing to the presence of copper

555   Ultramarine is the name given to a substance of a fine blue
lour which was first obtained from the *lapis lazuli*, in which it occurs
ixed with a colourless matrix, and has been used as a valuable
gment   From analysis, aluminium, silicon, sodium, and sulphur are
und to be the chief constituents, and in 1828 Gmelin succeeded in
eparing a blue dye-stuff of the nature of ultramarine by treating
umina with Glauber's salt, silicic acid, and charcoal   Since then, the
mmercial preparation of this colour, which is distinguished by its
changeableness in light and by its beauty, has grown to a large in

dustry. Kaolin is heated with Glauber's salt, or soda, charcoal, and sulphur, at first with exclusion of air, and the dull-green coloured product is then roasted with sulphur, with access of air, whereupon the blue colour develops. A series of different colours, from red-violet to blue-green, is obtained by varying the relative amounts of the original substances and the method of treatment. The ultramarine is made ready for use by washing with water and levigation.

While ultramarine is stable to light and air, even in the presence of lime, it is decomposed even by *weak acids*, thereby becoming colourless and evolving *sulphuretted hydrogen*.

In spite of its having long been known, and of the technical preparation of ultramarine having been practised for many years, the chemical nature of this substance is not yet clear. The sodium in it can be replaced by silver and potassium; so far it behaves like a salt. Its formula, however, is not known, since we have as yet no means of separating the pure substance from any impurities it contains.

* 556. **The other Earth Metals.** The elements already mentioned which are allied to aluminium, viz. scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, and ytterbium, along with a number of still less certain companions, are all of them very rare, and occur only in isolated parts of the earth's crust, in Scandinavia, and in North and South America. Their properties are similar to those of aluminium, subject to the same deviations as were found in the other groups, with increase of the combining weight; that is, the free metals are all the more readily oxidisable the greater their combining weight, and, in the same sense, the bases become stronger.

The *hydroxides* are white, amorphous precipitates, which, however, no longer dissolve in alkali hydroxides; the higher members are even able to form carbonates. With potassium sulphate they form double salts, which are slightly soluble in water, and almost insoluble in excess of potassium sulphate solution. The latter behaviour is due to the diminution of the solubility by the presence of the sulphanion (p. 447), and is by no means a peculiar property of these double salts. The composition of the double salts, however, does not correspond to that of alum, but is expressed by the formula $MK_2(SO_4)_2$. Further, in the higher members the property of forming more highly oxidised compounds or peroxides is found.

By reason of this close agreement in the properties, it is no easy matter to separate these elements, which generally occur mixed in nature, from one another. Nor are there any methods of separation applicable to them such as are employed for other analytical purposes, but one has to be content with partial separation on the basis of slight differences in solubility, of chemical equilibrium, and of decomposability, by repeated performance of which the object is more or less attained. In fact, almost every investigation which has been carried out with

parative thoroughness has shown that one or other of the sub-
... hitherto regarded as simple is a mixture, and the whole history
... development of this part of chemistry may be designated as the
... isolation of new individuals from the total amount. It is by
... means probable that these separations have already reached a
finite conclusion.

As characteristic of the various elements of this group, there is,
... of all the *combining weight*. By some method or other, a partial
... ration of the mixture of substances is effected, *e.g.* by partial
precipitation of the salt solution with insufficient ammonia, and this
method is repeated until the combining weight of the fractions obtained
... longer changes on further separation. Another very important
... tion is afforded by the *optical* properties. Many of these elements
give a very complicated spectrum on allowing the electric spark to pass
between carbon points moistened with solutions of their salts. Since,
under given conditions, each element possesses a perfectly definite
spectrum, it can be seen whether the spectrum changes by partial
separation. Where this is the case, we are certainly dealing with a
... The higher members also exhibit *absorption spectra*, some
of them also *emission spectra*. The former are obtained by allowing
white light to pass through solutions of the salt in question, and then
examining it with the spectroscope. Dark bands are then seen in
definite positions, which are also characteristic for the different elements.
Further, the oxides of the higher members, when heated to incandes-
cence, do not emit *continuous* light, as solid substances usually do,
but the emitted light is found by the spectroscope to consist of *isolated*
... similar to the light of incandescent gases. In this case, however,
they are much broader than in the latter case.

Another kind of optical phenomenon, the importance of which for
the characterisation of the elements has not yet been fully demon-
strated, consists in the *phosphorescence* produced by the *cathode rays*.
When electrical discharges of high potential are allowed to pass
through a highly vacuous space, rays of a special kind are emitted from
the cathode, which are propagated in straight lines, and which render
... as many substances with which they come into contact. The
light that is produced differs also in different substances ; still, differences
occur in cases where chemical differences are unknown, so that it
does not appear safe to draw conclusions from the one as to the
other.

Scandium, yttrium, and *lanthanum* yield colourless salts, and form
only one oxide, of the composition M_2O_3. Besides the trivalent
... ide $Ce(OH)_3$, whose salts are colourless, *cerium* yields a tetra-
valent hydroxide, $Ce_2(OH)_8$ (and a corresponding oxide, CeO_2), which
... its salts, whose solutions are brown. We have here, therefore,
the salts of ions whose chemical composition is not different, but
which have different properties, depending on the different valency.
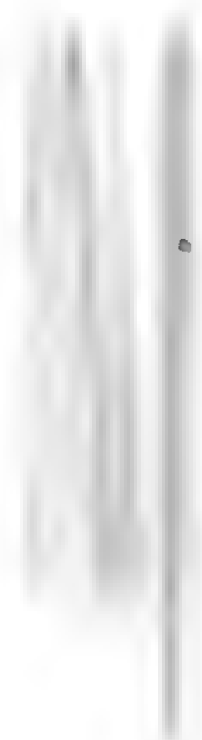
CHAPTER XXVII

IRON

1. General.—Metallic iron was not obtained from its naturally occurring compounds at so early a date as some of the other metals, especially copper and tin. This is due to its high point of fusion, and to the much greater difficulty in obtaining it in the metallic state from its compounds. Thus, in prehistoric times iron does not appear until after bronze, i.e. mixtures containing copper as essential constituent, and was apparently at first a great rarity.

Notwithstanding the wide distribution of iron, it scarcely ever occurs in the metallic state on account of its tendency to form compounds with oxygen and sulphur. The chief occurrence of metallic iron, except in some rather accidental cases through the action of chemical processes connected with volcanic activity, is in certain *meteorites*. These are masses which do not originally belong to the earth, but which, in the course of their flight through space, approach so closely to the earth that, owing to atmospheric friction, they lose their kinetic energy, which is thereby converted into heat, and fall to the earth. Many of these masses consist of iron.

Masses of native iron also occur, although rarely (e.g. at Ofvivak in Greenland), whose meteoric origin is doubtful, although no explanation has been given of any other possible origin.

Iron is a grey, tenacious metal, which fuses with great difficulty, at about 1600°. It combines with free oxygen quickly at high temperatures, slowly at low ones. In the heat essentially compounds of the formula Fe_3O_4 to Fe_2O_3 are formed; in the cold, iron hydroxide $Fe(OH)_3$ is formed. The hydrogen necessary for this is taken up in the form of water. In fact, iron "rusts" or oxidises at a low temperature only in moist, not, or not measurably, in dry air. Since the rust does not adhere, it does not protect the iron against further oxidation (p. 3).

At all temperatures water is decomposed by iron. The decomposition of water by red-hot iron is a classical experiment (p. 83). Even at the ordinary temperature decomposition takes place with evolution

571

of hydrogen, but exceedingly slowly, so that the evolution of hydrogen can be observed only by using large surfaces (iron powder). Iron is dissolved even by the weakest acids, thereby passing into divalent *diferrous* with evolution of hydrogen.

The combining weight of iron has been found to be Fe = 55.9

558. Commercial Iron. Commercial iron is not pure, but contains up to as much as 5 per cent of carbon, which has a very great influence on its properties, and also smaller quantities of other impurities. While pure iron, although very tenacious, is comparatively soft, its hardness increases with the amount of carbon it contains and its behaviour at moderately high temperatures becomes essentially different.

There are three chief kinds of commercial iron, viz. *wrought iron*, *steel*, and *cast iron*, the first contains the smallest, the last the highest amount of carbon. Wrought-iron approximates most nearly both in composition and in properties to *pure* iron; it is tough, not very hard, and on being heated first becomes soft like wax or sodium before melting. This property is of the greatest importance for the technical working of iron, as it renders it possible to shape the metal and to unite different pieces without it being necessary to raise the temperature to the melting point of the metal. On the contrary, it is sufficient to heat to the temperature of softening (about 600), so as to attain the object by pressing, rolling, and forging. The uniting of the two pieces of iron by pressure (hammering) is called *welding*. The temperature necessary for this is bright red heat.

The properties of wrought-iron do not undergo essential change when it is heated and suddenly cooled. The character of *steel* how ever, depends in the highest degree on such treatment.

Steel is iron which contains from 0.8 to 2.5 per cent of carbon, but is otherwise as pure as possible. The carbon is chemically combined with the iron, and this carburetted iron or iron carbide FeC is alloyed with the rest of the iron. The result of the presence of this foreign substance is, in the first place, an appreciable sinking of the melting point; at 1100 steel is liquid and can be cast. Cast steel is a metal consisting of fine crystalline grains, which, like wrought iron, softens before melting, and can therefore be forged. By such treatment steel acquires a fibrous or sinewy character, similar to wrought iron. If the steel is made red-hot and then suddenly cooled, it becomes brittle, and at the same time acquires its highest degree of hardness. It is then so hard that it scratches glass, and is hence called *glass hard*. If this steel is again carefully heated, all degrees of hardness can be imparted to it, for it increases in softness the longer or the higher it is heated. This process is called the *tempering* of steel.

As an index of the degree of tempering to be attained, use has been made from olden times of the colours which a bright steel surface acquires on being heated. At about 220°, the metal begins to oxidise

with a measurable velocity, and the oxide produced forms a
ting on the metal. If the thickness of this coating is of the
a wave length of light, the corresponding interference colours,
colours of thin plates," begin to appear. Since the shortest
visible waves, the violet, is first extinguished, the first tarnish-
to appear is the complementary colour, pale straw yellow.
then through the colours orange, purple, violet, blue, and finally
grey. To each of these colours there corresponds a definite
of hardness of the steel. Steel for tools to work iron is allowed
the yellow stage, for brass the purple red stage, while tools
are allowed to become blue. Although colour and hardness
exactly correspond, still the correspondence is sufficient for an
ed workman.

great utility of steel in the arts is due to the diversity in the
of hardness which it can acquire. In the soft state it can be
to any desired form, and the shaped objects can then be brought
degree of hardness.

is only in recent years that the theory of *tempering* has been
ear. Iron carbide, Fe_3C, mentioned above, is not only itself
rd, but it forms with pure iron a homogeneous mixture, a
solution,' which is also hard; so much the less hard, the less
it contains. If, now, such a solid solution, consisting at higher
tures of carbide and iron, is *slowly* cooled, it breaks up at about
to pure iron and iron carbide, which exist as a conglomerate
side. Since pure iron is soft, it imparts this property also to
ure.

, however, the cooling is performed *rapidly*, the breaking up of
solution does not occur, and the latter therefore preserves its
. The solid solution hereby becomes metastable or to a certain
supersaturated

his explains, in the first place, why quenched steel is hard,
owly cooled steel is soft. The *tempering* of hard steel, now,
in the separation of the solid solution into its two constituents
elevation of the temperature, the separation occurring all the
pidly the higher the temperature. By sudden cooling, the
the mixture attained at any point is preserved, since, at the
temperature, the velocity of change is immeasurably small.
responding degree of hardness is then obtained.

These considerations also make clear the fact, learned by experi-
at the temper depends not only on the temperature but also
time, in such a way that a lower temperature for a long period
same effect as a higher temperature for a shorter time.

tempering can be carried out in one operation by appropriately
to above 670 until the desired mixture of iron and solid solu-
the equilibrium between which alters with the temperature is pro-
and then fixing this state by suddenly cooling. The temperature

of hydrogen, but exceedingly slowly, so
can be observed only by using large st
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necessary for obtaining a definite degree of hardness depends on the amount of carbon present. If this is known, the temperature required to produce a given degree of hardness can be decided beforehand.

If the amount of carbon increases to from 4 to 5 per cent, the melting point of the iron becomes still lower, and the metal loses its toughness and the power of assuming the fibrous condition, but it still retains the power of being tempered to a certain degree. Such iron is called *cast-iron*.

Two kinds of cast iron are distinguished, *white* and *grey*. The former is obtained by quickly cooling; it is very hard and crystalline and contains the greater part of its carbon chemically combined as carbide. When the cast-iron is slowly cooled, part of the carbon separates out in fine lamina as *graphite*, which imparts a grey colour to the iron. At the same time the metal becomes less hard and brittle and the grain finer. In this condition cast iron is used for innumerable purposes where ease in the shaping of the object by casting has to be taken into account, and where the smaller resistance of the metal to pulling strain and bending is no essential drawback.

559. The Ions of Iron. Iron forms *two* kinds of elementary as well as a large number of complex ions containing other elements along with the iron. We shall in the first place treat of the former.

The elementary ions of iron are di- and trivalent; the former is called *diferrion*, the latter *triferrion*, and all the compounds which are derived from the former are designated ferrous compounds, in contradistinction to those derived from the latter, which are designated ferric compounds. The ferrous compounds possess a similarity to those of magnesium, the ferric to those of aluminium.

Diferrion in the pure state is almost colourless. Most of the salts which contain diferrion exhibit a greenish coloration, which is usually regarded as that of the diferrion. It appears, however, to be due for the greatest part to the presence of a trace of triferrion, since dark-coloured compounds of the two exist which even in very small amount produce the green coloration.

Although *diferrion* does not absorb the visible rays to any great extent, it absorbs those of *great* wave length, the ultra-red or the heat rays, in a very pronounced degree. A vessel with parallel walls, filled with the solution of a ferrous salt, is the most effective means of freeing light rays (*e.g.* in projection apparatus) from the dark heat rays which are present, and thus of avoiding the harmful heating of the objects. The same property is possessed by glass containing ferrous silicate.

Diferrion has an "inky" taste, *i.e.* the taste of ink is due to the presence of iron, which is chiefly in the form of diferrion.

The salts of *diferrion* are, as already mentioned, very similar to those of *magnesium*, and are in many cases isomorphous with them; like the solutions, they have a greenish colour. The general reactions

... that this salt

... iron or iron sul-
... till it crystal-
... Iron sulphide
... moist state this is
... ferrous sulphate,
... The rock containing
to the air and moistened;
... large quantities of ferrous
... method of preparation is
... to use the iron vitriol for

... or "oil of vitriol" from iron
... air or "roasted," whereby it
... sulphate: $4FeSO_4 + O_2 + 2H_2O =$
... this latter salt decomposes into
... ferric oxide, in accordance with
... $H_2SO_4 + SO_3$. The resulting
... sulphur trioxide, on account of the
... moist air (p. 286); it therefore con-
... I," in contradistinction to the non-
... chambers, which does not contain
... was prepared in fairly large quan-
... Harz, it was also called *Nordhausen*

... method is no longer used, as the manu-
... by the contact method has completely

... ate, ferrous sulphate unites with potassium
... isomorphous with this, to form monoclinic
... type $K_2Fe(SO_4)_2 . 6H_2O$. The *ammonium*
... which crystallises well and does not oxidise
... lysis (cf. Manganese).

... rous **Salts**. — *Ferrous chloride*, $FeCl_2$, is a salt
... soluble in water, and which in solution rapidly
... the laboratory it is obtained in large quantities
... sulphuretted hydrogen from iron sulphide and
... on concentrating the solutions it is obtained in
... crystals containing $6H_2O$, which very readily
... the air with brown crusts of basic ferric salt.
... is obtained in the anhydrous state by heating
... of hydrogen chloride. The latter is decomposed
... hydrogen, and the ferrous chloride sublimes at
... in white-grey, lustrous scales, which feel like
... salt dissolves in water with great evolution of he

from it. The reaction $2FeI_2 - I_2 \; 2FeI$, therefore, does not take place completely, but the reverse reaction can also occur to a large extent. If the iodine is removed from the equilibrium, the reverse reaction must take place more and more, and ferrous iodide must ultimately remain. The reaction, however, becomes increasingly difficult the more iodine is removed from the solution.

Writing the ions which are present, the equation runs $2Fe$ $2I' - 2Fe' - I_2$, and the reader may be referred to the considerations set forth on p. 576.

* This reaction is used for analytical purposes for the separation of iodine from chlorine and bromine. For this purpose excess of a ferric salt is added to a solution containing the halogens as ions, and the liquid is distilled. The iodine then passes off with the steam, while the bromidion and chloridion remain behind. The volatilised iodine is absorbed in a solution of potassium iodide, and titrated with thiosulphate.

* A mixture of ferrous and ferric iodides is obtained as an intermediate product in the preparation of potassium iodide. Iodine and iron, in the proportions $3Fe : 8I$, are mixed with water, whereby all is dissolved, and the solution is precipitated with caustic alkali or potassium carbonate. Potassium iodide is formed in the solution, and the iron is deposited as the black ferrosoferric oxide (p. 582), when it can be more easily filtered and washed than the other oxides of iron.

567. Ferric Fluoride, FeF_3, is distinguished by the fact that it is extremely slightly dissociated into its ions, and does not, therefore, exhibit the reactions of triferrion and fluoridion. It is a difficultly soluble, white compound, which forms with the alkali fluorides compounds of the type of cryolite (p. 563), constituting the alkali salts of a trivalent fluoferranion, FeF_6'''.

568. Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by adding to a solution of ferrous sulphate half as much sulphuric acid as is therein contained, and evaporating the solution with addition of nitric acid (to oxidise the diferrion to triferrion). After heating the residue there is finally obtained a yellowish-white powder, which apparently does not dissolve in water. If left for some time under water, however, it dissolves in abundance, and fairly concentrated solutions can be prepared. It is a salt, therefore, which has a very small *solution velocity*.

The solutions appear brown red, but the colour is all the paler the more free acid is added. This is due to hydrolysis, which is diminished by free acid. The hydrolysis again increases when the solution is greatly diluted.

Ferric sulphate crystallises along with potassium or ammonium sulphate to form alums, which are called *iron alums*. The salt crystallises in octahedra, which generally appear violet (probably owing to the presence of a trace of manganese). When pure the salt is

almost colourless, tinged with yellow. Iron alum is generally used where it is necessary to employ a ferric salt in cases where ferric chloride, for some reason, cannot be used.

569. Ferric Thiocyanate, $Fe(SCN)_3$, is exceedingly soluble in water, and in the undissociated state is of a deep red-brown colour. The smallest amount of triferrion, therefore, can be detected by adding an excess of thiocyananion (e.g. potassium thiocyanate) to the solution. Since the reaction is due to the undissociated ferric thiocyanate (for both thiocyananion and triferrion are colourless, or only slightly coloured), it will, ceteris paribus, be all the more distinct the greater the amount of the undissociated compound present.

* This object is, in the first instance, attained by a large excess of thiocyananion. If to a solution containing only a very little triferrion, only an equivalent amount of thiocyananion is added, the coloration produced is very feeble; it becomes more pronounced the more the concentration of the thiocyananion is increased. Further, the reaction becomes more distinct if the liquid is shaken with ether. Ferric thiocyanate in the undissociated state is soluble in ether; the undissociated portion, therefore, passes for the greater part into the ether, a fresh amount of the compound is formed in the aqueous solution, and this also goes into the ether. When equilibrium is finally established there is much more undissociated ferric thiocyanate in the ether than there was previously in the aqueous solution. As a consequence, the sensitiveness of the reaction is correspondingly enhanced.

* If a concentrated solution of sodium or ammonium sulphate is added to a liquid coloured red with ferric thiocyanate, the red colour becomes weaker, and finally disappears. This is due to the fact that owing to the presence of a large amount of sulphanion, the triferrion is used up for the formation of undissociated ferric sulphate, which is not coloured. The salts of monobasic acids do not act so strongly, since the ferric salts of the polybasic acids are generally much less dissociated than those of the monobasic acids. Fluorides act very strongly (cf. p. 584).

570. Other Ferric Salts.—*Ferric acetate* is an unstable salt, the behaviour of which is, for analytical purposes, of interest. If sodium acetate (or acetanion in any other form) is added to the solution of a ferric salt, the liquid becomes dark red in colour, owing to the formation of *undissociated* ferric acetate. This reaction is used as a reagent for acetic acid, but similar colorations are produced by a number of other anions, so that the reaction is not unequivocal. If the red solution is heated it becomes turbid, and a precipitate of basic acetate is formed, which contains all the iron. In this way iron (in the ferric state) can be precipitated from acid solutions, which is of importance for many separations

* If the liquid is again allowed to become cold in contact with the precipitate, it slowly regains its red colour, and the iron begins to pass

into solution. When, therefore, an exact separation is required, the precipitate must be filtered hot.

* The explanation of this reaction is the same as in the case of aluminium acetate (p 567) Since acetic acid is a weak acid (the hydrion of which is still further diminished by the excess of acetate from the sodium acetate added), hydrolysis largely occurs, and in the heat this goes so far that ferric hydroxide, or basic acetate, is precipitated The reverse process takes place at a lower temperature on account of diminution of hydrolysis.

571. Ferric Phosphate, $FePO_4$, is precipitated from a solution of a ferric salt, acidified with acetic acid, by the addition of sodium phosphate, as a white, slimy precipitate which, unlike most of the other phosphates, is not appreciably soluble in acetic acid. That property is also made use of in analysis.

572. Sulphur Compounds of Iron. If iron and sulphur are heated together a black mass of the composition FeS is formed. This we have already got to know as the starting substance in the preparation of sulphuretted hydrogen. The compound can be prepared in any desired amount by raising the end of an iron bar to a red heat, lowering this into a large crucible, and adding sulphur in lumps. The two elements combine with so great a rise of temperature that the iron sulphide is melted, and the preparation can be continued by simultaneously adding more sulphur and pushing the iron bar farther in.

* A hydrated sulphide of iron of a black colour is formed when sulphur and iron filings are mixed in the proportions 32 · 56, moistened with water, and allowed to stand. The reaction commences slowly, but is accelerated by the heat produced, and in the case of large quantities it may be so violent that the mass becomes incandescent. Such experiments were formerly often made in imitation of volcanic phenomena. Since, however, the lava of the natural volcanoes does not consist of iron sulphide, it is only a case of external resemblance

Iron sulphide is readily decomposed by acids, with formation of ferrous salt and *sulphuretted hydrogen* (p. 273), and it is therefore not formed when sulphuretted hydrogen is passed into solutions of ferrous salts. By means of *ammonium sulphide*, however, a black precipitate of hydrated iron sulphide is formed in ferrous solutions ; when finely divided it appears green-black, and forms a very sensitive reaction for iron. Iron sulphide rapidly oxidises in the air, ferrous sulphate being first formed (p. 578), so that it cannot be washed on the filter without beginning to dissolve.

Iron sulphide occurs native as *magnetic pyrites* in yellow-brown masses, with a metallic lustre. These have very nearly the composition of the simple iron sulphide, but always contain a slight excess of sulphur. How this deviation from the law of constant proportions is to be interpreted has not yet been explained.

copper belongs to the next group: this is due to the fact that this salt is also partially isomorphous with the other vitriols.

Iron vitriol can be prepared by dissolving metallic iron or iron sulphide in dilute sulphuric acid and evaporating the liquid till it crystallises. It is, however, usually obtained in another way. Iron sulphide occurs very widely distributed in nature. In the moist state this is oxidised on contact with oxygen and passes into ferrous sulphate, according to the equation $FeS + 2O_2 = FeSO_4$. The rock containing iron -sulphide is therefore spread out exposed to the air and moistened; in a short time, by extracting with water, large quantities of ferrous sulphate can be obtained from it. This method of preparation is so cheap that it was formerly the custom to use the iron vitriol for the preparation of sulphuric acid.

In order to obtain sulphuric acid or "oil of vitriol" from iron vitriol, the salt was first heated in the air or "roasted," whereby it was converted into basic ferric sulphate: $4FeSO_4 + O_2 = 2H_2O + 4FeSO_4(OH)$. On being heated, this latter salt decomposes into sulphuric acid, sulphur trioxide, and ferric oxide, in accordance with the equation $2FeSO_4(OH) = Fe_2O_3 + H_2SO_4 + SO_3$. The resulting mixture of sulphuric acid and sulphur trioxide, on account of the presence of the latter, fumes in moist air (p. 286), it therefore constituted "fuming sulphuric acid," in contradistinction to the non-fuming acid prepared in the leaden chambers, which does not contain anhydride. Since this fuming acid was prepared in fairly large quantities at Nordhausen in the Harz, it was also called *Nordhausen or vitriol acid.*

At the present time this method is no longer used, as the manufacture of sulphur trioxide by the contact method has completely ousted all the others.

Like magnesium sulphate, ferrous sulphate unites with potassium sulphate and the salts isomorphous with this, to form monoclinic double sulphates of the type $K_2Fe(SO_4)_2 . 6H_2O$. The *ammonium* salt $NH_4)_2Fe(SO_4)_2 . 6H_2O$, which crystallises well and does not oxidise in the air, is used in analysis (cf. Manganese).

Other Ferrous Salts. — *Ferrous chloride*, $FeCl_2$, is a salt which is very readily soluble in water, and which in solution rapidly oxidises in the air; in the laboratory it is obtained in large quantities in the preparation of sulphuretted hydrogen from iron sulphide and hydrochloric acid. On concentrating the solutions it is obtained in the form of greenish crystals containing $6H_2O$, which very readily become coated in the air with brown crusts of basic ferric salt.

Ferrous chloride is obtained in the anhydrous state by heating iron in a current of hydrogen chloride. The latter is decomposed with liberation of hydrogen, and the ferrous chloride sublimes at a bright red-heat in white grey, lustrous scales, which feel like talc. The anhydrous salt dissolves in water with great evolution of heat.

Concerning *ferrous bromide* and *ferrous iodide*, there is nothing special to note. The aqueous solutions of these salts are readily obtained by bringing the free halogens together with excess of metallic iron; these salts are very readily soluble.

Ferrous carbonate, $FeCO_3$, occurs naturally as a valuable iron ore — *spathic iron ore*. It crystallises in rhombohedra which are isomorphous with those of calc-spar and of magnesite; in the pure state it is almost colourless, but is generally coloured yellow-brown from incipient oxidation. From aqueous solutions of ferrous salts soluble carbonates precipitate it as a greenish-white substance, which readily dissolves in acids, with effervescence, and which also becomes rather rapidly brown owing to oxidation.

563. Ferric Hydroxide. —By the addition of bases to solutions of ferric salts, ferric hydroxide, $Fe(OH)_3$, is obtained as a brown, flocculent precipitate, which is very slimy when precipitated in the cold. If the liquid is heated along with the precipitate, the latter acquires a firmer character, and can be readily filtered.

Ferric hydroxide is a very weak base, and is practically insoluble in water. In acids it is soluble when freshly precipitated, and if it has not been heated; it passes, however, into less soluble forms even on standing for some time in the heat, partial anhydride formation presumably occurring. On being heated to a red-heat it loses water and is converted into ferric oxide, Fe_2O_3, according to the equation $2Fe(OH)_3 = Fe_2O_3 + 3H_2O$. This ignited iron oxide is almost insoluble in acids, and passes into solution only on being warmed for days with concentrated hydrochloric acid; it dissolves more quickly when it is at the same time reduced to ferrous salt.

Ferric hydroxide possesses the property to a very high degree of forming *colloidal solutions*. These are obtained by dissolving freshly precipitated ferric hydroxide in a concentrated solution of ferric chloride, whereby soluble basic salts are formed, and dialysing this through a partition of parchment paper into pure water. The aqueous solutions of ferric chloride, like those of all other ferric salts, are partially hydrolysed into free acid and colloidal ferric hydroxide. Since hydrochloric acid diffuses very quickly, while ferric hydroxide and basic ferric chloride can hardly penetrate the parchment paper, the hydrochloric acid present first of all passes out. The chemical equilibrium of hydrolysis is thereby disturbed, more hydrochloric acid must be split off, and this is in turn removed by diffusion. These reactions continue until finally only or almost only colloidal ferric hydroxide is left in the dialyser.

The solution so obtained is of a dark blood-red colour, and exhibits the characteristic properties of colloidal solutions in the most distinct manner. It does not possess electrical conductivity to any considerable extent; its boiling point and freezing point, also, differ only inappreciably from those of pure water. Addition of electrolytes pro-

late it, the ferric hydroxide separating out as a flocculent mass. Chemical reactions do not take place with it, or do so only very slowly; more especially, it exhibits none of the analytical characteristics of the ferric salts, which will be mentioned later, since it does not contain interion. On standing with hydrochloric acid it gradually passes into a liquid possessing the properties of the solution of ordinary ferric chloride.

Solutions of colloidal ferric hydroxide are prepared in the above manner for medicinal purposes, and are sold under the name *ferrum oxydatum dialysatum* (dialysed iron).

Both hydroxide and oxide of iron occur in nature; both are important iron ores, and are called brown iron ore and hæmatite respectively. The former occurs in brown-black lustrous masses, which, on being ground, yield a *yellow-brown powder*. Iron oxide crystallises in rhombohedra which are isomorphous with those of corundum (p. 560), and have a black metallic appearance; in this form it is called *iron glance*. The concretionary iron oxide (kidney ore) has a lustrous black appearance similar to brown iron ore; on being ground, however, it gives a *red* powder.

Iron oxide and hydroxide are extremely widely distributed in nature. In the primitive rocks, iron regularly occurs in the form of silicate, in the weathering, the silicic acid is removed and the hydroxide remains. This mixes with all sedimentary rocks, and imparts to them a yellow-brown to red colour. When reducing actions occur, as, for example, through admixture with organic substances, the ferric hydroxide is reduced to the dark-coloured compound mentioned on p. 577, and this gives a grey-blue or greenish-blue colour to the particular substances. This colour is frequently seen in the case of clays containing iron; when these are "fired" the organic substance is destroyed, and the iron passes into ferric oxide, whereby the previously blue clay becomes of a red colour.

Ferric hydroxide resembles aluminium hydroxide in many respects, especially in the fact that the salts of both have a similar composition, and are also mostly isomorphous. Like aluminium hydroxide, ferric hydroxide is completely precipitated by ammonia from solutions of ferric salts. It differs, however, from aluminium hydroxide in the fact that it is not dissolved by strong bases; in fact a method of separating the two hydroxides can be based on this difference. The method, however, is not very exact, for the difference, or the inability of ferric hydroxide to form anions containing oxygen (p. 560), is only one of degree; in very concentrated solutions of the alkali hydroxides, ferric hydroxide dissolves quite appreciably, and for this reason caustic alkalis prepared in iron boilers almost always contain iron. On diluting the solutions, the compound decomposes and the ferric hydroxide is gradually deposited as a brown precipitate on the bottom of the vessel.

In the presence of many organic substances, such as tartaric acid,

sugar, glycerine, etc., all of which contain several hydroxyl groups, ferric hydroxide is not precipitated by alkalis from solutions of ferric salts ; on the contrary, clear brown liquids are formed which exhibit the reactions of iron only imperfectly. The description of the compounds hereby produced belongs to organic chemistry ; they are salt-like compounds in which the iron is present not as cation but as part of a complex anion. They have received mention here from the fact that they are extremely readily formed, and when formed they render the analytical detection and the precipitation of the iron more difficult. In such cases the organic substance must be destroyed, which is most easily done by strongly heating.

564. Magnetic Iron Ore.—Ferric oxide unites with ferrous oxide to form a compound which occurs abundantly in nature, and is a very valuable iron ore : $Fe_2O_3 + FeO = Fe_3O_4$. It is called *magnetic iron ore*, as it frequently exhibits a strong natural magnetism ; the chemical name is ferrosoferric oxide.

Magnetic iron ore crystallises in regular octahedra, and is isomorphous with *spinel* (p. 561), which consists of aluminium oxide and magnesium oxide, $Al_2O_3 + MgO$. As can be seen, the two compounds are constituted after the same type, since both contain one combining weight of a monoxide, MO, to one of a sesquioxide, M_2O_3. In the present case, however, iron is the only metal present, its divalent form taking the place of magnesium, and its trivalent form that of aluminium. In magnetic iron ore, therefore, both the isomorphic relations come simultaneously into force.

If ferrous salt and ferric salt be mixed in such proportions that there is twice as much iron in the case of the latter salt as in the former, and the mixture be poured into excess of caustic soda, a black granular precipitate is obtained, which may be looked upon as a hydroxide of the above compound. A salt-forming base, also, appears to exist ; this is a compound of ferrous and ferric hydroxide, and to it is due the greenish colour of the ferrous salts. This compound, however, if it exists, is very unstable, its salts decomposing almost completely into mixtures of ferrous and ferric salts.

565. Ferric Salts.—*Ferric chloride*, $FeCl_3$, is obtained by heating iron in a current of chlorine. It then sublimes as dark green crystals with a metallic lustre, and is much more easily volatile than ferrous chloride.

These crystals dissolve in water with great rise of temperature and yield a yellow-brown solution from which the anhydrous salt cannot be again obtained by evaporation and heating. Four different hydrates containing from $6H_2O$ to $2H_2O$ crystallise out, according to the temperature, and on attempting to drive off the last traces of water by heating, hydrogen chloride is eliminated at the same time, and iron oxide remains behind.

Hydrated ferric chloride can be obtained by dissolving ferric oxide

their ions   Since an increase in the positive charge is equivalent to a decrease of the negative, the following ions correspond to one another:

Diferrion Fe·· and Ferrocyanidion Fe(CN)₆''''.
Triferrion Fe··· and Ferricyanidion Fe₂(CN)ₘ'''.

This correspondence is also given expression to in the names.

The general properties of the ferricyanides are similar to those of the ferrocyanides. In these compounds, also, neither the reactions of triferrion nor those of cyanidion can be detected. A difference, however, is shown in the reactions with iron salts.

If diferrion and ferricyanidion come together, a blue precipitate is formed which is very similar to Prussian blue, but has a somewhat different composition. For the salt which is formed, *ferrous ferricyanide*, has the composition Fe₃[Fe(CN)₆]₂, or in sum Fe₅(CN)₁₂. It contains, therefore, 2·40 combining weights of cyanogen to one of iron, while Prussian blue contains 2·53 combining weights of cyanogen to one of iron.

No precipitate is produced with ferric salts, but the liquid only becomes somewhat darker in colour. Ferric ferricyanide is soluble in water, and in the undissociated state is dark coloured.

By means of concentrated hydrochloric acid, hydroferricyanic acid, H₃Fe(CN)₆, can be liberated from the solution of its salts, and can be obtained in brown needles which are readily decomposable and very readily soluble in water.

The ferrous compound is decomposed by alkalis in the same way as Prussian blue, for potassium ferrocyanide and ferric hydroxide are formed, and not potassium ferricyanide and ferrous hydroxide, as one would expect. This is due to the fact that the potassium ferricyanide primarily formed is reduced by the ferrous hydroxide, which is a very strong reducing agent, to the ferrous compound, the ferrous hydroxide being converted into ferric hydroxide.

576 **Other Complex Compounds**.—With many other substances besides cyanogen, iron is capable of forming complex compounds which contain compound ions in which iron is present, and therefore do not give the reactions of iron, or do so only very incompletely. The description of most of these substances must be omitted here; only a few of them, which, for some special reason, chiefly analytical, are of importance, can be mentioned here.

In the first place, there must be mentioned the compounds which are formed when *nitric oxide* or higher oxygen compounds of nitrogen are brought together with ferrous salts. The latter compounds are then reduced to nitric oxide, and this unites with the diferrion to form the compound ion FeNO··. This is, however, rather unstable, for it undergoes decomposition even on boiling the solution, nitric oxide escaping and diferrion being again formed. This behaviour is

made use of for the preparation of pure nitric oxide from mixed gases. On it also analytical methods of detecting nitric oxide and the higher oxy compounds of nitrogen depend (p. 327)

Further, the complex iron anions can be formed by the compounds of ferric hydroxide with organic (and also with some inorganic) substances containing hydroxyl, which were mentioned on p 581. They are recognised by the fact that their solutions are not precipitated by alkalis.

577. Oxalates of Iron.—The oxalates of iron, which have from all time been regarded as a chemical puzzle on account of the differences of their colour from the ordinary colours of the ferrous and ferric compounds, must also be reckoned among the complex compounds.

When free oxalic acid is added to a ferrous salt, a crystalline precipitate of ferrous oxalate, difficultly soluble in water, is deposited. Unlike the other ferrous salts, this is not greenish but orange coloured, like a ferric salt. It dissolves with a strong yellow-red colour in an excess of potassium oxalate, and from this solution the salt $K_2Fe(C_2O_4)_2$ can be obtained in crystals In the solution, therefore, a salt of the complex ferro-oxalanion, $Fe(C_2O_4)_2''$, is formed.

* The solution of potassium ferro-oxalate, which is prepared at the moment it is to be used by mixing solutions of ferrous sulphate and normal potassium oxalate, is, on account of its powerful reducing properties, used in photography for developing silver bromide plates.

Moist ferric hydroxide readily dissolves in oxalic acid to yield a liquid which, unlike the other ferric salts, is coloured green. The colour is, however, emerald green and not pale green, like that of the ferrous salts. From the solution, badly crystallising ferric oxalate can be obtained, which readily decomposes. If, however, another oxalate is added, fine crystalline, green coloured salts of the complex ferro-oxalanion, $Fe(C_2O_4)_3'''$, are obtained, e.g. $K_3Fe(C_2O_4)_3$.

The solutions (also coloured green) of these salts possess in a high degree the property of *sensitiveness to light*. In sunlight, a solution of ferric oxalate almost instantaneously deposits a yellow precipitate of ferrous oxalate, and carbon dioxide is evolved: $Fe_2(C_2O_4)_3 = 2Fe(C_2O_4) + 2CO_2$ The salts of ferrioxalic acid behave in a similar manner, being converted into the corresponding salts of ferrooxalic acid: $2K_3Fe(C_2O_4)_3 = 2K_2Fe(C_2O_4)_2 + K_2C_2O_4 + 2CO_2$. These phenomena are made use of for the production of photographs, especially of platinum pictures, a graded reduction being allowed to take place by exposure under a "negative," and the potassium ferro-oxalate thus produced being used for the reduction of platinum from a compound present The solution has also been used as a chemical photometer i.e. an apparatus for measuring the strength of the chemically active light. Apart from other objections, the results are of little value

from the fact that every sensitive substance has its particular range of
light waves which it absorbs and makes use of for chemical reactions.
There is, therefore, no such thing as a "chemical intensity of light"
in the absolute sense, and every chemical photometer indicates the
strength of only a definite range of rays of the light subjected to
examination, this range being dependent on the nature of the
photometer.

778. Iron Carbonyls. Carbon monoxide combines with iron to
form very remarkable compounds, which are slowly formed when the
two components come into contact at the ordinary or at a slightly
higher temperature. Various substances are hereby formed, contain-
ing from 4 to 7CO to 1Fe, which on cooling condense to brownish
coloured liquids; they are readily volatile, so that they mix in the
gaseous state with the excess of carbon monoxide. Their velocity of
formation is so small that even by using finely divided iron with a
large surface, only very small amounts are formed, which are difficult
to isolate and to prepare pure.

Appreciable amounts of these compounds are formed in iron
pipes which convey gas rich in carbon monoxide, especially when the
pipes are long and the carbon monoxide has, therefore, time to
unite with the iron. While for ordinary purposes these traces of iron
in the gas are of no importance, they have proved very inconvenient
in the application of such gas for *incandescent light*, as the iron oxide
which is produced in the combustion is deposited on the incandescent
mantles, and impairs their illuminating power.

A better known example of such compounds will be described
under nickel

779. Catalytic Actions of Iron. Both in the ionic state and
in various compounds, iron frequently exercises a very considerable
catalytic influence, especially on oxidation processes. To observe this
it is only necessary to mix dilute solutions of hydrogen peroxide
and hydrogen iodide, or better, potassium iodide plus acetic acid.
A reaction slowly occurs in which iodine is liberated and can be
rendered visible by means of starch. If quite a small amount of
a ferrous salt is added, the blue coloration occurs incomparably
more quickly. A similar accelerating action has been proved in the
case of many other reactions.

At the present time, no regularities of a more general nature are
known respecting these relations. It is of importance, however, to be
aware of them, since the physiological importance of iron probably
depends on them. The presence of iron has been detected both in
the red blood corpuscles and in the green colouring matter of the
assimilating plant cells (i.e. those which reduce carbon dioxide in
light), and although at the present time the laws of these relations
cannot be stated, nevertheless the fact above mentioned indicates an
important direction for investigation.

2 Q

580. **Thermochemistry of Iron.**—The heats of formation the most important compounds of iron are :—

Diferrous Fe	94 kj
Triferrous Fe	39 ,,
Ferrous hydroxide Fe OH$_2$	571 ,,
Ferric hydroxide Fe$_2$OH	829 ,,
Ferrosoferric oxide Fe$_3$O$_4$	1107 ,,
Ferrous chloride FeCl$_2$	343 ,,
Ferric chloride FeCl$_3$	402 ,,
Ferrous sulphide hydrated, FeS – H$_2$O 100 kj.	

581. **Metallurgy of Iron.** As metallic iron does not occur native to any great extent, the very large quantities of this metal which are used in the industries must be manufactured from compounds. For this purpose the oxygen compounds, which are reduced with charcoal, are almost exclusively used.

This reduction is carried out chiefly in the blast furnace, which an upright, elongated, egg-shaped space enclosed by masonry. In this alternate layers of iron ore and coal, along with the additions necessary for the production of a readily fusible slag, are introduced from the top. In the lower part of the furnace there is a narrow cylindrical space into which heated air is blown, and in which the fused iron collects.

The changes which the ore undergoes in such a furnace are very varied. In the upper parts it is only heated, whereby water is eliminated from hydrated ores, carbon dioxide from iron carbonates, and the ores are converted into ferric oxide or ferrosoferric oxide. In the lower, hotter parts of the furnace, this is reduced to metallic iron by the carbon monoxide which is present in abundance. Since the temperature is not nearly high enough to melt the iron, the reduced, spongy metal sinks down along with the excess of charcoal to the lowest part of the furnace, where the highest temperature is reached through the combustion of the charcoal in the injected air. The iron here combines with carbon and fuses together, forming cast iron or crude iron, and collects at the bottom of the furnace.

The iron is run off from time to time and formed into long blocks, or used for making castings. The slag which is formed at the same time, and which is essentially a mixture of various silicates, floats on the fused iron, and can continually run off through an overflow.

The crude iron obtained in this way contains, besides about 4 per cent of carbon, silicon, phosphorus, sulphur, and also manganese in varying amounts. For the conversion of this into wrought iron or steel, not only must the amount of carbon be reduced, but the other admixtures, which diminish the value of these other kinds of iron, must be removed as far as possible.

For this purpose, several methods are employed, which differ from

be another, however, only in the technical details, but which all amount to the same thing chemically, viz. the removal of the foreign substances by *oxidation*. The chemical reactions are most readily intelligible in the *Bessemer process*, which is at present chiefly used

The iron is introduced in the fused state into a large pear-shaped vessel, and heated air is blown through the molten mass. The impurities then burn more rapidly than the iron, and the products of oxidation pass off in the gaseous state, or pass into the slag which is simultaneously formed. While, in this manner, carbon, silicon, and sulphur can be readily removed, the removal of the phosphorus was not successful as long as there was used for the vessel a lining which consisted essentially of clay. Not until this was replaced by a *basic* lining consisting of lime or magnesia, whereby the phosphorus passes into the slag as the corresponding *phosphate*, did it become possible to obtain good wrought-iron or steel from crude iron rich in phosphorus. The slag rich in phosphoric acid which is thereby formed, is used as an important fertiliser in agriculture (p. 532), and is called *Thomas slag*, after the inventor of the method

The course of decarbonisation by the Bessemer process, which takes place in a very short time, can be controlled by spectroscopic observation of the flame produced, and can be interrupted at the desired moment. If 2 per cent of carbon is still left in the iron, steel is formed ; if the amount of carbon is reduced to 1 per cent, and less, a kind of wrought-iron is obtained which is called ingot iron.

CHAPTER XXVIII

MANGANESE

582 General.—The element manganese is very closely related to iron. It differs from it in being more readily oxidised, and in its higher compounds being more readily formed than in the case of iron. For the rest, the corresponding compounds of manganese and iron are very similar to one another, and in many cases are isomorphous.

In nature, manganese occurs very widely distributed, but is much less abundant than iron. It is found chiefly as *manganese peroxide* MnO_2, the many applications of which we have repeatedly noted.

In its chemical relations, manganese is characterised by the very great diversity of its compounds. It forms not less than five oxidation stages, the lower members of which form bases, the higher acids. There is, accordingly, a correspondingly large number of different salts containing manganese. By reason of this it exhibits very diverse relations of affinity and isomorphism; whereas the lowest series of compounds is allied to magnesium, the following ones exhibit isomorphic relations with aluminium, titanium, sulphur, and chlorine.

The combining weight of manganese is $Mn = 55 \cdot 0$.

583. Metallic Manganese.—Pure manganese was formerly little known. The metal fuses with still greater difficulty than iron, and, like the latter, it unites at a high temperature with carbon, so that the element obtained by the reduction of the oxygen compounds with charcoal always contains a fair quantity of carbon. Manganese free from carbon can now be readily obtained by reduction with aluminium, according to the method of Goldschmidt, and manganese is thus found to be a reddish grey, lustrous metal which is harder than iron and keeps very well in the air, whereas the carbonised metal which was formerly known oxidised very rapidly. It is very readily dissolved by acids, and in this respect probably takes the first place among the heavy metals; even in dilute acetic acid it evolves hydrogen with great vigour. By the dissolution, the corresponding manganous salt is formed.

Manganese is not used in the free state, but is employed in large

antities as an addition to iron. White crude iron (p. 574) generally ntains larger or smaller amounts of it. Such an iron is especially itable for being treated by the Bessemer process, as the great heat oxidation of manganese facilitates the maintenance of the requisite gh temperature.

584 **Dimanganion.**—The first series of compounds which manese forms, is derived from the divalent ion Mn, which, in many pects has a great similarity to magnesium. Dimanganion has a pale dish colour, no special physiological action, and its heat of forma s 210 k_j. All soluble manganous salts are distinguished from ferrous salts by the fact that they do not oxidise in the air in acid ution.

585. **Manganous Hydroxide,** $Mn(OH)_2$, is obtained as a reddish ite precipitate when a solution of a manganous salt is precipitated th alkalis. In the air, this precipitate rapidly becomes brown, reby passing into manganic hydroxide, $Mn(OH)_3$. It is not dis ved by excess of alkalis, but is so by ammonium salts. The reason exactly the same as in the case of magnesium hydroxide (p 541). e degree of solubility, also, is about the same. The ammoniacal lution however, behaves differently in so far as it rapidly becomes own and turbid in the air. This is due to the absorption of oxygen, ereby manganic hydroxide is formed, which is much too weak a se to be soluble in ammonium salts.

By heating the carbonate or by precipitating hot, the anhydride, manganous oxide, MnO, is obtained in the form of a greenish powder.

Of the manganous salts, the *chloride,* $MnCl_2$, may in the first place mentioned. It is obtained in the impure state as a residue in the reparation of chlorine from manganese peroxide or pyrolusite (p 169). is a pale reddish, easily soluble salt, which crystallises with $4H_2O$.

586 **Manganous Sulphate,** $MnSO_4$, crystallises generally in ark reddish crystals with $4H_2O$; besides this, it can crystallise with $7H_2O$ in the forms of ferrous sulphate, with $5H_2O$ in the forms of opper sulphate, etc. With the alkali sulphates, also, it forms mono-inic double salts of the type $K_2SO_4 . MnSO_4 . 6H_2O$

587 **Manganous Carbonate,** $MnCO_3$, can be obtained as a dish precipitate, by precipitating manganous salts with carbonates; it ses in the air, but much less rapidly than the hydroxide. In ture the carbonate is found as *manganese spar* this occurs in mbohedra, which are isomorphous with those of calc spar

588 **Manganous Sulphide,** MnS, is the most soluble of the phur compounds of the heavy metals which are formed in aqueous ution. It is decomposed even by acetic acid, and can, therefore, be precipitated from solutions of manganous salts with sulphuretted drogen, but only with alkali sulphides. If the precipitation is rried out in the cold, a slimy, flesh coloured precipitate (the only phur compound of this colour is obtained; from moderately con

centrated solutions in the heat, anhydrous manganous sulphide is sometimes precipitated, under conditions which are not yet exactly known, as a grey green powder. In the air the sulphur compound oxidises very rapidly, so that it must be washed with a solution of ammonium sulphide when use is made of it for the precipitation of manganese in analysis.

589. **Manganous Borate** is obtained by the precipitation of a manganous salt with borax, and is placed on the market in the form of a brown powder. It is used in large quantities for the preparation of varnish. This is due to its catalytic properties. There are certain vegetable oils, e.g. linseed oil, which oxidise in the air to resinous masses. With the crude oils, this oxidation takes place only slowly; if, however, the oil is heated and a small quantity (less than 1 per cent) of manganous borate is added, the absorption of oxygen is greatly accelerated catalytically, and a rapidly drying oil or a varnish is obtained. Further, dimanganion has the property of very greatly increasing the action of certain organic catalysers which accelerate oxidation, the "oxidases."

590. **Manganic Compounds**.—The compounds of trivalent manganese or the manganic compounds, are formed from the manganous compounds by oxidation. Even in the case of iron a considerable diminution of the basic properties accompanied the corresponding transformation, a fact which found expression in the incipient hydrolysis of the salts; in the case of manganese, however, the difference is much greater. The hydrolysis of the manganic compounds in aqueous solution is so great that such compounds are quite unstable, and rapidly decompose with separation of manganic hydroxide, Mn(OH)₃.

For this reason, very little is known regarding the properties of the ion Mn⁺⁺⁺. Its colour appears to be violet-red, and the dark brown colour of some solutions of manganic salts is the result of hydrolysis, since the manganic hydroxide is dark-brown in colour.

The normal hydroxide does not occur in nature, but various anhydrides of it do. The partial anhydride MnO(OH) is called manganite, manganese sesquioxide, or the complete anhydride, Mn₂O₃, is called braunite, and Mn₃O₄ hausmannite.

In the solid state, some of the manganic salts are known as well-defined compounds. The sulphate is obtained by warming manganese peroxide with concentrated sulphuric acid until it has dissolved to a dark-coloured liquid, and then washing the paste of sulphate, which is formed even in the heat, free from sulphuric acid by means of nitric acid. It is a dark green powder, which dissolves in water with a violet-red colour, which very speedily changes to brown, manganic hydroxide being deposited. Manganic chloride, MnCl₃, is also formed temporarily, when manganic hydroxide is dissolved in cold concentrated hydrochloric acid, and on dilution with water behaves like the sulphate.

Those manganic salts, however, which are not ionised to any great extent, undergo only a slight hydrolysis, as was to be foreseen according to the theory of hydrolysis. To these there belongs, in the first instance, the fluoride, MnF_3, which can be prepared by dissolving manganic hydroxide in aqueous hydrofluoric acid, and which can be obtained in dark red crystals. This forms double salts with the alkali fluorides, of the type $K_2F_2 \cdot MnF_3 \cdot 2H_2O$.

Finally, the phosphate, $MnPO_4$, appears to be a slightly dissociated salt. It dissolves in excess of phosphoric acid to a red-violet liquid, which is stable even at the temperature of boiling.

591 **Manganese Peroxide**.—Tetravalent manganese forms the hydroxide $Mn(OH)_4$, the anhydride of which is the oft-mentioned manganese peroxide, MnO_2. Since even in the case of trivalent manganese the basic properties had practically disappeared, it is natural that tetravalent manganese is no longer capable of forming salts like a base. On the other hand, the acid properties which are present in a pronounced manner in the higher stages of the manganese compounds, begin to be indicated here.

Manganese peroxide occurs fairly abundantly in nature as *pyrolusite*, and is the most important of all the naturally occurring compounds of manganese. It occurs in grey-black crystals, the powder of which is black (not brown).

The *hydroxide*, $Mn(OH)_4$, is obtained by subjecting manganous salts to strong oxidising actions in neutral or alkaline liquids. As an oxidising agent there can be used chlorine, bromine, or a hypochlorite. The hydroxide is dark brown in colour, and amorphous, and passes readily into the colloidal state. By moderate dehydration, the intermediate anhydride, $MnO(OH)_2$, which has the same appearance, is obtained.

If the hydroxide is treated with cold, concentrated hydrochloric acid, it dissolves with a dark brown-green colour; if the solution is immediately diluted with a large quantity of water, the hydroxide is again deposited. This is due to the formation of a tetrachloride, $MnCl_4$, which is hydrolysed by much water. If the solution is warmed, it becomes colourless and evolves chlorine; manganous chloride remains in the residue. The reaction for the preparation of chlorine given on p. 169 takes place, therefore, in two stages, tetrachloride being first formed and then decomposing into chlorine and dichloride. The equations are $MnO_2 + 4HCl = MnCl_4 + 2H_2O$, and $MnCl_4 = MnCl_2 + Cl_2$.

The manganese perhydroxide prepared as above given, generally gives too little oxygen on analysis. This is due to the fact that the compound, $MnO(OH)_2$ or H_2MnO_3, can act like an *acid*, corresponding to carbonic acid or sulphurous acid, and form salts. If the manganese peroxide is formed in presence of a base, all the manganese passes into this compound; in the absence, however, of another base, part of

the manganese in the divalent state is incorporated in the precipitate, the manganous salt of the above acid, *manganous acid*, the formula of which is $Mn . MnO_3$, equal to Mn_2O_4, being formed. If, however, a base is present, e.g. lime, *calcium manganite* is formed, and all the manganese passes into the tetravalent state

* This reaction is made use of for the *regeneration* of the manganese liquors in the manufacture of chlorine from hydrochloric acid and pyrolusite. The requisite amount of lime is added to the liquor, in order to convert the manganous chloride into manganous hydroxide, and still one combining weight of lime more. If air is blown through this mixture, oxidation takes place rapidly and readily, and calcium manganite, $CaMnO_3$, is deposited as a black precipitate, known as Weldon mud. This again yields chlorine with hydrochloric acid but half as much hydrochloric acid more is required, as can be seen from the equation $CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + Cl_2$

* At the present day this method is being more and more given up, as the electrolysis of the alkali chlorides yields more chlorine than can be made use of in the arts.

Besides being used for the preparation of chlorine, manganese peroxide is employed in pottery works for the production of brown and violet colours   Melts to which manganese peroxide has been added are coloured violet ; if iron is present at the same time, a dark brown colour is produced.

Manganese peroxide is also employed in the manufacture of glass. It is there used in order to remove the greenish coloration which the glass assumes owing to the presence of ferrous compounds (p. 599). The action is probably due to an oxidation of the ferrous to the ferric compound, the yellow colour of which is much feebler. Besides this, the yellow colour of the ferric glass is counteracted by the violet colour of the manganese salt, and an imperceptible neutral tint is produced

* Glass which has been decolorised with manganese exhibits the remarkable property that it slowly becomes red violet in colour when exposed to light   This colour passes through the whole mass of the glass, but is absent from those parts where the light was weakened, as for example, behind letters fixed on shop windows. This phenomenon is a proof that in spite of the apparently solid nature of the glass, chemical processes can occur in the interior of the mass, as in a system which is not in equilibrium.

* Manganese peroxide is also used for making galvanic cells, since it conducts the electric current, and as a cathode gives a fairly high potential with zinc as anode. The processes taking place in galvanic cells will be discussed in detail at a later point in connection with a simpler case (Chap XXXII) : at this point it will be sufficient to state that such cells are generally formed of an oxidising agent and a reducing agent, separated from one another by an intermediate con

generally a salt solution, and where necessary, a porous
—. On making the proper connection, an electric current is
—ed whereby the reducing agent is oxidised at the expense of
—ising agent ; the chemical energy which thereby becomes free
—the work necessary for the electric current In the above cell
—ed of manganese peroxide and zinc, the manganese peroxide is
—ising and zinc the reducing agent Both these are immersed
—ution of sal ammoniac, and when the circuit is closed the zinc
—s and the manganese peroxide is reduced to manganous oxide.
—uch a cell can be easily made as follows. A mixture of
—ite and coke (for the sake of the conduction) is placed at

—ttom of a tumbler, a rod of
—onducting charcoal is introduced
—his, and the glass filled with a
—a of ammonium chloride ; a zinc
—suspended in the upper part
—liquid in such a way that it
—ot touch the manganese per
—and the charcoal (Fig. 116) On
—the zinc and the charcoal by
—of a conductor, an electric current
—through the latter. Such a cell
—ché cell) lasts for a long time
—small, intermittent currents are
—from it, as, e.g., for electric
—for strong, continuous currents

Fig. 116

—eless, because the necessary chemical reactions do not occur
—tly rapidly, and the cell therefore quickly loses its electro-
—force when much used. It recovers its electromotive force on
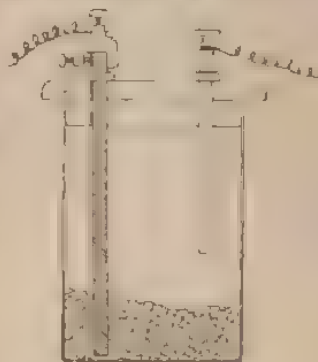
—ignition, manganese peroxide loses oxygen, and is converted
—nganoso-manganic oxide, Mn_3O_4, corresponding to ferrosoferric
— The reaction is $3MnO_2 = Mn_3O_4 + O_2$. This was formerly the
—by which oxygen was prepared in the pure state, and it has
—e a certain historical importance.

—same manganoso-manganic oxide, although not of exactly con-
—mposition, is formed when any of the other oxides of manganese
—gan or carbonate is ignited in the air, and this form is therefore
—r weighing manganese in analytical separations. As has been
—ed, however, the composition is not quite constant ; this depends
—pecially on the temperature, the amount of oxygen decreasing
—at as the temperature rises

—. **Mangananion and Permangananion.** Although com
—of a pentavalent manganese are not known, manganic acid,
—, can be regarded as a partial anhydride of the hydroxide of
—ert manganese, for $Mn(OH)_6 - 2H_2O = MnO_2(OH)_2 = H_2MnO_4$.

This interpretation, however, is in the first instance only a for... for neither is the hexahydroxide itself nor compounds cor... sponding to it known. It will be found, however, that th... tation is a convenient one in discussing the oxidation and r... processes of the manganese compounds.

Free *manganic acid* is not known; it is no more possible to ... it pure than it is to prepare thiosulphuric acid, for its sa... exist along with hydrion in solution without at once underg... formation. It is known only in its salts, which are stable in ... solutions, but in neutral or acid solutions are immediately c... into permanganation. The analyses of the salts, and, more... the pronounced isomorphism of these with the sulphates, lea... formula MnO_4 for the anion, and H_2MnO_4 for the acid.

The salts of manganic acid, or the *manganates*, are very e... formed by heating any manganese compound with strong bas... carbonates. If potassium or sodium carbonate (or better, a m... of these) is heated to fusion and a trace of manganese is ... added to it, the latter dissolves with absorption of oxygen fr... air and imparts a fine dark-green colour to the melt. On more... mass appears almost black when a fair amount of manganese... sent, and greenish-blue when only very little is taken. The re... is so sensitive that it can be used for the detection of mangan... crude potashes, patches of a blue green colour are frequent... due to accidental traces of manganese, which on heating hav... converted into manganate.

" In order to prepare potassium manganate, a mixture of... lusite and caustic potash is heated in the air; oxygen is t... absorbed, and a black mass of potassium manganate is formed ... this is dissolved in water a dark green, almost opaque solution ... even with very small amounts.

" The isomorphism of manganese with sulphur is seen when ... sium sulphate is added to the above solution, and this allowe... crystallise. The crystals of potassium sulphate are obtained, ev... in all tints of bright and dark green.

The solution of the crude potassium manganate remains unch... when it contains a large amount of potash. On adding any ac... solution acquires a fine red colour, and then contains another comp... which is derived from *septivalent* manganese. The same colo... occurs on allowing the dilute solution to stand in the air; the ... change is then effected by the carbon dioxide of the air. In p... from green to red, the solution passes through a number of in... mediate violet and blue colours, and this change of colour has gi... for the substance the name "mineral chameleon."

On adding a fairly large excess of ordinary caustic potash ... solution after it has become red, the colour again changes fairly ra... to green.

When the red-coloured liquid is evaporated, a salt crystallises out in almost black crystals with a metallic lustre, the composition of which is represented by the formula $KMnO_4$. Apparently, therefore, it contains the same ions as potassium manganate, only in different proportions, there being, in the present case, only one combining weight of potassium to one of the ion MnO_4', instead of two as in the case of the manganates. This, however, furnishes the essential distinction between the two compounds, a distinction which is similar to that between ferrocyanide and ferricyanide. The ions of potassium manganate are $2K^{\cdot}$ and MnO_4''; those of the red salt, which is called *potassium permanganate*, $K^{\cdot}$ and MnO_4'. Whereas, therefore, the former ion, MnO_4'', is similar to that of divalent *sulphanion*, the composition of the latter, MnO_4', is such as to make it more comparable with that of the monovalent *perchloranion* ClO_4'. As a matter of fact, the two are isomorphous, and if potassium perchlorate is allowed to crystallise in presence of some potassium permanganate, mixed crystals are obtained varying from bright to dark red in colour : this can be seen with especial ease and distinctness under the microscope.

Permanganic acid can be regarded as a partial anhydride of *heptavalent* manganese, for, $Mn(OH)_7 = 3H_2O + HMnO_4$. In agreement with what was set forth on p. 348, permanganic acid has, accordingly, to be regarded as a higher stage of oxidation of manganese than manganic acid, and must therefore be formed from the latter by means of oxidising agents. As a matter of fact, the transformation takes place most smoothly when chlorine is passed into the solution of the manganate, for the following reaction then takes place : $2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$. The equation of the ions is, $2MnO_4'' + Cl_2 = 2MnO_4' + 2Cl'$. The reaction therefore consists in the transfer of one negative charge from MnO_4'' to the chlorine.

In the transformation of the manganates into permanganates in acid solution, a portion of the mangananion acts as an oxidising agent, the manganic acid being reduced to manganese peroxide.

The reaction may, for example, be written $3K_2MnO_4 + 4HNO_3 = 2KMnO_4 + 4KNO_3 + MnO_2 + 2H_2O$. It is, however, more instructive to write it so as to show only the reacting ions. We then have $3MnO_4'' + 4H^{\cdot} = 2MnO_4' + MnO_2 + 2H_2O$. This shows that hydrion is used up in the process, and thus explains why it takes place in acid solution.

That the reverse transformation from permangananion to manganinion takes place in alkaline solution is to be attributed, on the one hand, to the consumption of hydroxidion, which, of course, takes place more easily in solution containing a large quantity of hydroxyl. The reducing action which is at the same time necessary is probably occasioned by organic substances, which are generally present dissolved in the caustic potash. Whether, in accordance with the equation $4MnO_4' + MnO_2 + 4OH' = 3MnO_4'' + 2H_2O$, permangananion along with

manganese peroxide can change into manganination with consumption of hydroxyl, has not yet been sufficiently investigated

In contradistinction to manganic acid, permanganic acid is very stable in acid solution. An aqueous solution of permanganic acid can be obtained by decomposing the barium salt in dilute solution with sulphuric acid. A red solution is thus obtained which looks like that of any permanganate whatever, and which conducts electricity like an equivalent solution of hydrochloric acid. Permanganic acid is therefore a *strong* acid, whose aqueous solutions are largely dissociated even at a moderate dilution.

Of the salts of permanganic acid, the most important is the potassium salt already mentioned, as it is not very readily soluble and crystallises well, and can therefore easily be prepared pure. It is manufactured on the large scale, and in recent times to a large extent by electrolytic oxidation

Pure permanganic acid, $HMnO_4$, is not known, but its *anhydride* Mn_2O_7, is. It is obtained as a brown-green, oily liquid, which separates out in drops by carefully adding concentrated sulphuric acid to dry potassium permanganate; it is very volatile. Even at the ordinary temperature it is converted into a red-violet, readily decomposable vapour which, on slight provocation, decomposes with explosion into oxygen and manganese peroxide, the latter floating around in brown, cobweb-like flakes

The permanganates are very powerful *oxidising agents*, and are used as such. Fairly large quantities are used in the chemical industry, especially for the oxidation of organic substances. To the same property is due its application for purposes of disinfection, treatment of wounds etc.

The mode of action of permangananion in oxidation varies according as it is employed in acid or in alkaline solution. In the former case a manganous salt is formed, in the latter manganese peroxide. Since the latter is a higher stage of oxidation than dimanganion, the oxidation action is more fully taken advantage of in the former case than in the latter.

The oxidising action is so powerful that almost all organic substances are attacked by permanganate. The hydrated manganese peroxide which is thereby formed separates out on the substances and colours them dark brown. On account, therefore, of the resulting decomposition, solutions of permanganates must not be filtered through paper nor kept in contact with indiarubber, cork, or such substances *

* The brown coloration can be readily removed by means of sulphurous acid; soluble manganous sulphate is thereby formed: $MnO_2 + SO_2 = MnSO_4$ [1]

² The same reaction also takes place even in the absence of water

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[1] In part, also, manganese dithionate is formed: $MnO_2 + 2SO_2 = MnS_2O_6$ (?) the latter is formed chiefly when crystalline peroxide is used, and at a low temperature.

is therefore made use of in order to remove sulphur dioxide from gas mixtures.

The solutions of the permanganates can all be readily identified by their fine red-violet colour. On examining the transmitted light by means of the prism, five fairly sharp absorption bands are seen lying between the yellow and the green. With equivalent solutions, these bands have exactly the same position and character for all permanganates; they are shown also in exactly the same way by free permanganic acid. This proves that we are dealing here with a definite property of permanganonion, MnO_4', which remains independent of the other ion present at the same time in the solution. Since these bands can be measured with great exactness, it has been possible in this case to prove the identity with great strictness.

Potassium permanganate is employed in analytical chemistry. For since its solutions are so strongly coloured that even very small quantities can be recognised, a method for the volumetric determination of reducing agents has been based on the fact that, on oxidising with permanganate, the red colour disappears so long as reducing substance is still present. So soon as this has been used up, even a very slight excess of permanganate can be recognised by the permanence of a red coloration.

This method is chiefly used for the determination of iron, since in acid solution this is immediately converted, even in the cold, from diferrion to triferrion. Since the manganese in passing from permanganonion to dimanganion sinks from the heptavalent to the divalent stage, five oxidation units are available. With these, five combining weights of diferrion can be oxidised to triferrion, since for each combining weight only one unit is necessary. If the liquid is imagined acidified with sulphuric acid, the equation, when written in the usual manner runs: $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$. Omitting the non-essential ions, we obtain the much more simple equation: $5Fe\cdot\cdot + MnO_4' + 8H\cdot = 5Fe\cdot\cdot\cdot + Mn\cdot\cdot + 4H_2O$.

The determination is performed by placing the solution of permanganate in a burette furnished with a glass stop-cock and allowing it to run into the solution of the ferrous salt. Since the method depends on the oxidation of diferrion to triferrion, all the iron which it is desired to determine must be present as diferrion. In order to attain this, or, as the case may be, to make sure of this, the acid liquid is treated with metallic zinc, whereby any triferrion which may be present is converted into diferrion, a corresponding amount of zinc passing into solution: $2Fe\cdot\cdot\cdot + Zn = 2Fe\cdot\cdot + Zn\cdot\cdot$. The permanganate solution is allowed to flow into the solution until the last drop gives a pink coloration to the liquid. The liquid must be maintained fairly strongly acid, as a large amount of hydrion is used up in the reaction. Hydrochloric acid, however, must not be used, since this is partially oxidised to chlorine, and too much permanganate is therefore required.

* It is only in the presence of triferrion that this oxidation of chloric acid takes place in sufficient amount to cause an error in analysis. If no iron is present, it is possible even to warm solutions of the two substances without appreciable action. We are therefore here dealing with a case of catalytic influence. presence of dimanganion greatly retards the oxidation of hydrochloric acid by permanganate; it, therefore, for other reasons, iron is to be titrated with permanganate in hydrochloric acid solution, it is best to previously add an abundance of manganous sulphate.

Besides being used for the determination of iron, permanganate chiefly employed for the titration of *oxalic acid* and nitrous. The former thereby passes into carbon dioxide, and we have the equation $5C_2O_4'' + 2MnO_4' + 16H = 10CO_2 + 2Mn'' + 8H_2O$. In equation, C_2O_4 is the ion of oxalic acid. If it is desired to write equation with respect to undissociated oxalic acid, it is only necessary to unite the corresponding 10H' with the $5C_2O_4''$, and we have $5C_2O_4H_2 + 2MnO_4' + 6H = 10CO_2 + 2Mn'' + 8H_2O$. In the state of affairs, this other method of writing the reaction makes difference.

This method is used not so much for the determination of acid (which can be more conveniently determined by means of as for the estimation of oxalates, *e.g.* calcium oxalate. On account of the great sensitiveness of the reaction, much smaller quantities calcium oxalate can be determined with permanganate than by and the method is, therefore, employed where as accurate determination as possible of very small quantities has to be made.

The volumetric determination of nitrous acid is also carried acid solution, and takes place in accordance with the equation $2MnO_4' + 5NO_2' + 6H = 2Mn'' + 5NO_3' + 3H_2O$. The reaction does not place instantaneously, and, of course, occurs all the more slowly as concentration of the nitrous acid decreases during the reaction.

Finally, the use of permanganate for the determination of *manganese itself* in the form of dimanganion, must be mentioned. When the two ions meet in feebly acid solution, they undergo double decomposition to manganese peroxide, which is deposited as a brown precipitate. If the precipitation is carried out in the heat, the precipitate settles sufficiently quickly, so that the supernatant liquid at becomes clear, and it can be seen whether it is coloured by excess of permanganate. We obtain the equation of the reaction we consider that all the manganese is converted into the tetravalent form. Each combining weight of dimanganion must therefore take two units, while the heptavalent manganese of permanganation gives up three units. Two molecules of permanganation, therefore, react with three molecules of dimanganion, and we have $3Mn'' + 2MnO_4' + 4OH' = 5MnO_2 + 2H_2O$.

Hydroxyl is therefore used up in the reaction, and the liquid

some acid if we started with a neutral solution. In strongly acid solution the reaction does not occur. Further, pure manganese peroxide is formed only when a base is present which can combine with it to form a manganite (p. 600). All these conditions are fulfilled if the precipitation is carried out in presence of an excess of *zinc oxide*.

503 General Remarks on Oxidising and Reducing Agents.
All oxidising agents can (in the presence of water) be formally regarded as hydroxyl compounds, and all reducing agents as hydrogen compounds of the particular elements. The formulæ of these hydroxides and hydrides are chosen such that they are obtained by the addition of the elements of water to the various substances. In the case of manganese, for example, we have —

Manganous series	$Mn(OH)_2$ divalent
Manganic series	$Mn(OH)_3$ trivalent
Manganese peroxide	$MnO_2 + 2H_2O = Mn(OH)_4$ tetravalent
Manganate series	$H_2MnO_4 + 2H_2O = Mn(OH)_6$ hexavalent
Permanganate series	$HMnO_4 + 3H_2O = Mn(OH)_7$ heptavalent.

As an example of a series of reducing agents, we choose the compounds of sulphur. Taking sulphuric acid, the hydrogen compound of SO_4, as the initial substance, we have the following formulæ:

Sulphuric acid		$SO_4 . H_2$
Sulphurous acid	$H_2SO_3 - H_2O$	$SO_4 . H_4$
Sulphur	$S + 4H_2O$	$SO_4 . H_8$
Sulphuretted hydrogen	$H_2S + 4H_2O$	$SO_4 . H_{10}$

In order, therefore, to oxidise sulphuretted hydrogen, for example, to sulphuric acid, $10 - 2 = 8$ oxidation units must be taken up. If the oxidation is to be carried out in acid solution with permanganate, whereby dimanganion is formed, there are, for each molecule of permanganate, $7 - 2 = 5$ oxidation units available, and since 8 and 5 have no common factor, 5 parts of sulphuretted hydrogen must be used to 8 parts of permanganate.

In order to complete the equation, we must consider that the ions produced, viz. 8 molecules potassion and 8 molecules dimanganion, require together 24 equivalents of anion, of which 5 S yield only 10 as SO_4. Other 14 equivalents of some acid must therefore be added, e.g. $7H_2SO_4$. We therefore obtain the equation $5H_2S + 8KMnO_4 + 7H_2SO_4 = 8MnSO_4 + 4K_2SO_4 + 12H_2O$, or, leaving out the ions which remain unchanged,

$$5H_2S + 8MnO_4' + 14H' = 5SO_4'' + 8Mn'' + 12H_2O.$$
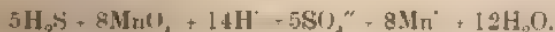
An important point is with regard to the alteration of the acid or basic condition of the reaction mixture in the process, for in general such a change takes place in oxidations, and we have to ask how this is to be calculated. The answer is practically contained in the above

examples, still it may be useful to describe the method in detail. It
is as follows. Making use only of the elements of water besides the
reacting substances, one examines whether after writing the equation,
obtained from the consideration of the oxidation values, excess of acid,
or excess of hydroxide appears on the right-hand side. If from this
point of view we write the equation for the oxidation of sulphuretted
hydrogen with permanganate, we obtain—

$$5H_2S + 8KMnO_4 + 2H_2O = 4K_2SO_4 + MnSO_4 + 7Mn(OH)_2.$$
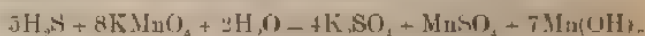
Besides the neutral salts, therefore, $7Mn(OH)_2$ are formed, or 14
equivalents of hydroxyl remain unsaturated, and as many equivalents
of an acid must therefore be added in order that the same acid or basic
condition may be produced as before the reaction.

The calculation becomes still more simple in the following way.
From the practically neutral sulphuretted hydrogen the dibasic sulphuric
acid is formed; since $5H_2S$ are oxidised, this corresponds to an increase
of the acid by 10 equivalents. On the other hand, 3 equivalents
of base are formed from the neutral permanganate, viz. one monovalent
potash and one divalent manganous hydroxide. The $8KMnO_4$, there-
fore, make the reaction mixture more basic to the extent $3 \times 8 = 24$
equivalents. Subtracting the 10 equivalents of acid from this, there
remains a basic excess of 14 equivalents, and for these a correspond-
ing amount of acid is necessary in order to maintain the condition
unchanged.

In oxidation and reduction processes, therefore, a change in the
neutrality, or, more generally, in the acid or basic condition, generally
occurs. If hydrion is used up in the reaction, this will, in accordance
with the law of mass action, take place all the more readily the more
hydrion is present, or the more acid the solution is. The same holds
good when hydrion is not used up, but hydroxidion is formed. For
since the latter unites with hydrion to form neutral water, the two
processes are equivalent in the presence of water. If, on the contrary,
hydrion is formed in the process, the latter will take place better in
the presence of hydroxidion, and will be retarded or rendered practically
impossible by the presence of hydrion. In both cases, indeed, chemical
equilibria are established. Very frequently, however, these equilibria
are so much towards the one side of the reaction equation that it is
not possible to detect the presence of the substances on the other side.

An example of this is afforded by the transformation of manganate-
anion into permanganation, and *vice versa* (p. 602). Since in the case
of the direct change hydrion is used up, corresponding to the equation
$3MnO_4'' + 4H = 2MnO_4' + MnO_2 + 2H_2O$, the transformation will be
promoted by the presence of hydrion, and the solution will contain
permanganate. If the hydrion is decreased by the presence of a large
amount of hydroxidion, the mangananion is stable. Another example
is afforded by the behaviour of iodine in presence and absence of

hydroxidion. Free iodine reacts with hydroxidion to form iodanion and iodidion, in accordance with the equation $3I_2 + 6OH' \quad 5I' + IO_3' + 3H_2O$. In this reaction much hydroxidion disappears, and the reaction must therefore take place more easily when it is present; as a matter of fact, it takes place in alkaline solution, e.g. in a solution of caustic soda. If, however, hydrion is added, the reaction is reversed, and elementary iodine is again set free : $5I' + IO_3 + 6H \quad 3I_2 + 3H_2O$.

594. Complex Compounds of Manganese.—Manganese can form with cyanogen, compounds which are quite similar to those which we have already discussed in detail in the case of iron. In this case also we have the two series of compounds derived from a tetravalent manganocyanidion, $Mn(CN)_6''''$, and a trivalent manganicyanidion, $Mn(CN)_6'''$, and both are obtained in a manner similar to the corresponding iron compounds. They are both, however, less stable, and the manganicyanides, more especially, through their readiness to undergo decomposition, recall the salts of trivalent manganese.

Potassium manganocyanide, $K_4Mn(CN)_6 + 3H_2O$, is isomorphous with potassium ferrocyanide and crystallises in dark blue crystals, which, however, yield an almost colourless solution. Potassium manganicyanide, $K_3Mn(CN)_6$, is red, and is isomorphous with potassium ferricyanide. Its aqueous solutions decompose on being boiled, the manganese being deposited as manganic hydroxide.

CHAPTER XXIX

595. General. In many of its chemical peculiarities chromium is closely allied to the metals of the iron group, especially to iron and manganese. On the other hand, it is related to the elements molybdenum, tungsten, and uranium, which must be placed in the last group of metals, so that chromium could be grouped just as well with them. It is somewhat arbitrary, therefore, in which group it is placed; that it is here classed in the iron group is done for didactic reasons.

Chromium is closely related to manganese in the number of the series of compounds which it forms. Whereas, however, in the case of manganese, the acids corresponding to the higher stages of oxidation were somewhat unstable, these belong in the case of chromium to the most important and best-known compounds.

Chromium forms the following series of compounds:—

Salts of the divalent dichromion, $Cr^{..}$.
Salts of the trivalent trichromion, $Cr^{...}$, and complex compounds derived from it.
Chromium trioxide, CrO_3, and acids derived from it.
Chromium peroxide, whose composition is not yet known with certainty.

The combining weight of chromium is $Cr = 52.1$.

596. Metallic Chromium was for long known only in the form of an impure product containing carbon, since the fusion of pure chromium could not be effected on account of its high melting point. By the reduction of chromium oxide with aluminium, in accordance with a general method given by H. Goldschmidt, very pure metallic chromium is now manufactured in large quantities. It is used in the iron industry to add to steel (chromium steel).

* This preparation is carried out by mixing chromium oxide with aluminium powder, both carefully dried, and initiating the reaction with a small quantity of the mixture. For this a very high temperature is necessary; this is produced by mixing aluminium powder with

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...ium peroxide, forming a pill of this, and sticking a piece of ...esium ribbon into it. If the magnesium ribbon is ignited, which ...be done with a match, the combustion of the aluminium with the ...ygen of the barium peroxide begins, the mass thereby becomes white-..., and initiates the reaction in the neighbouring portions of the ...romium mixture In proportion as this undergoes transformation, ...e of the mixture is added; the temperature thereby soon rises so ...gh that the chromium fuses.

The method has the advantage that it does not require a specially ...lt furnace, but can be carried out in an ordinary crucible, prefer ...t one of magnesia; the outside of the crucible becomes only slowly ...on On account of the high temperature of fusion of chromium, ...e preparation of the fused metal is successful only when fairly large ...antities are employed, but then with ease.

A similar method is used for preparing other metals, and also ...r the production of very high temperatures. In the latter case cheap ...ates, generally iron oxide, are used. With such mixtures fusions, ...lting, etc., can be carried out on the spot with great ease and ...rtainty, so that the method is of great technical importance

Chromium is a lustrous white, very hard metal, the melting point ... which is about 2000°. Its density is 6.8. It remains unchanged ...the air; even at a red heat it becomes only slowly coated with a ...in layer of oxide, which exhibits the colours of thin plates. It is ...solved by dilute hydrochloric and sulphuric acids, with evolution of ...ydrogen. Nitric acid does not attack it, since it becomes "passive" ...that acid.

Chromium passes into this passive state, i.e. ceases to be attacked ...acids, even by lying in the air. The metal when in this state is ...ot attacked at the ordinary temperature by dilute acids. Treatment ...the metal with strong oxidising agents has the same effect. If the ...sive metal is allowed to lie for a fairly long time under acid, or if ...it is warmed, dissolution with evolution of hydrogen suddenly com ...ences If the metal is used as an anode (p. 195) in dilute acid, it is ...nverted by weak currents into its lowest compound, a chromous salt. ..., however, the strength of the current is increased, the metal suddenly ...gins to dissolve in the form of its highest stage of combination as ...romic acid The passive metal likewise becomes active, i.e. becomes ...uble in acids when it is touched with a piece of zinc or similar metal ...der acid

An explanation of these remarkable phenomena, sufficient in all ...rticulars, has not yet been found.

597. Chromous Compounds *Dichromium*, Cr, is coloured blue, ...d has a very pronounced tendency to pass into the trivalent tri ...mation It is a very strong reducing agent, and can even decompose ...ter with evolution of hydrogen The chromous salts can, therefore, ...obtained pure only with difficulty, and in aqueous solution cannot

be long kept without passing into chromic salts. They are easily obtained by dissolving metallic chromium in dilute acids; can also be prepared by the reduction of chromic compounds metallic zinc. From the solutions bases precipitate chromous hydroxide, $Cr(OH)_2$, as a yellow precipitate, which in the moist state into chromic oxide with evolution of hydrogen, and is oxidised immediately in the air. Through the spontaneous oxidation of chromous amalgam in the air, black *chromous oxide* is formed, which passes the green chromic oxide on being powdered.

From the solutions of the chromous salts excess of sodium precipitates difficultly soluble *chromous acetate*, a dark red, crystalline salt, which can be washed and dried if air is excluded; it is the only fairly stable chromous compound. The aqueous solution, prepared with the help of hydrochloric acid, is used for the absorption of free oxygen.

By igniting chromic chloride (*vide infra*) in a current of hydrogen white, difficultly volatile chromous chloride, $CrCl_2$, which dissolves water with a blue colour, is obtained.

598. Chromic Compounds.—*Trichromium* is violet coloured, in its properties is most nearly related to aluminium and iron with which it is isomorphous. It has also a highly developed tendency to form complex compounds of all kinds, some of which are violet, some green.

Chromic hydroxide is obtained as a blue-green precipitate by action of ammonia on solutions of the chromic salts, whereby a amount of the salt readily passes into complex ammonia compound. Chromic hydroxide precipitated with alkali hydroxide dissolves excess of the precipitant to a fine green-coloured liquid, in which corresponding *alkali chromite*, i.e. a salt of the anion $Cr(OH)_4$ contained. The solution, however, is very unstable; a less hydrated hydroxide of a green colour, which is less soluble than the one directly precipitated, separates out quickly when heated, and slowly in the Such phenomena have already been discussed in the case of beryllium and aluminium.

By partial dehydration various partial anhydrides are obtained from chromic hydroxide. One of these, of the composition $CrO(OH)$ is used as a pigment on account of its fine green colour. On igniting *chromic oxide*, Cr_2O_3, is formed; this can also be obtained in crystalline form by the decomposition of volatile chromium compounds, then crystallises in the form of corundum (p. 560) and forms green, lustrous rhombohedra.

Chromium oxide unites with oxides of divalent metals to substances of the type of *spinel*, which are found in regular crystals isomorphous with this substance. Of such compounds by far most important is chrome ironstone, a compound of chromium with ferrous oxide, $FeCr_2O_4$, which crystallises in black octahedra.

the compound of chromium most found. Chrome ironstone, therefore, forms the starting substance for the preparation of other chromium compounds.

Of the salts of the chromic series, we must first mention the *chloride*, which is obtained in the anhydrous state by heating chromium oxide and charcoal in a current of chlorine. It sublimes in the form of a fine violet red (peach-blossom red) substance, consisting of small lustrous scales, which appear to be insoluble in water. On very long contact, however, some passes into solution. The dissolution takes place very quickly, with appreciable rise of temperature, when some chromous chloride is added to the water. Other strong reducing agents have a similar action. A sufficient theory of this acceleration has not yet been given.

From the aqueous solution a green salt with $6H_2O$ is obtained, which cannot be directly converted into the anhydrous chloride, since, like the chlorides of all weak bases, it loses hydrochloric acid on being heated. The green solution is not to be regarded as the (partially hydrolysed) normal chloride with the ions $Cr^{...}$ and $3Cl'$, for on adding silver nitrate only $\frac{2}{3}$rds of the chlorine present is precipitated. The last third is therefore not present as ion, the solution also contains free acids. The chloride of a complex divalent cation containing chromium and chlorine, e.g. $ClCr''$, is therefore present. On standing for a lengthened period in dilute solution, the green colour of the solution changes to violet, and at the same time almost all the chlorine can be precipitated by silver nitrate. This corresponds to the formation of the normal chloride, which is accompanied by the production of the violet colour belonging to trichromion. On concentrating and heating the solution the green ion is again chiefly formed. None of these reactions are complete, and to each temperature and concentration there corresponds a definite equilibrium between the two forms. A solution containing almost solely the normal salt is obtained by dissolving the freshly precipitated chromic hydroxide in hydrochloric acid.

The two chlorides can be prepared in the solid state—the normal one by the crystallisation of the solution saturated with hydrogen chloride in the cold, the other in the heat. Both salts contain $6H_2O$; the normal salt is grey-blue, the other is green.

599. Chromic Sulphate, $Cr_2(SO_4)_3$, exhibits a similar variety of behaviour, and has been still more thoroughly investigated. From aqueous solutions the salt with $9H_2O$ is obtained, and its solutions exhibit the violet colour of the normal trichromion. If the solid salt is heated till it has lost about $3H_2O$, it becomes green. The solution, immediately after being prepared, exhibits a small conductivity, and contains therefore scarcely any ions. The conductivity increases very rapidly; but barium chloride gives no precipitate, which shows that no sulphanion is pre

contrary, various chromsulphuric acids, or their chromic salt
formed.

If mixtures of chromic sulphate and sulphuric acid in variou
portions are warmed, substances are obtained, the aqueous solutio
which give no reaction with barion, and therefore contain no
Neither do they exhibit the reactions of trichromion. They co
complex chromsulphuric acids. The amount of hydrion which
contain corresponds to the hydrion of the sulphuric acid added,
this way as much as $3H_2SO_4$ can be combined with $Cr_2(SO_4)_3$,
solutions are not stable, but soon decompose into their compon
the presence of the ions Cr''' and SO_4'' can then be detected

Chromic sulphate forms a regular alum, *chrome alum*, with pota
and ammonium sulphate, this crystallises in very large octahedr
a dark purple colour. If a crystal of chrome alum is suspended
saturated solution of ordinary alum and crystallisation allowed to
place, the dark octahedron is obtained regularly enclosed in a col
one. Such regularly zoned crystals are also a sign of isomorph
between the substances which can form them.

Chrome alum is generally prepared by the reduction of potas
bichromate (*vide infra*); it is used in dyeing and for many o
purposes. With animal glue the chromic hydroxide, which is spli
hydrolytically, forms a compound which is insoluble in hot wa
it has a "tanning" action on the glue. Use is frequently made
this property.

600. Sulphur Compounds of chromium cannot be prepared
the wet way. Sulphuretted hydrogen is without action on chromi
salts, and with ammonium sulphide *chromium hydroxide* is precipata
while sulphuretted hydrogen escapes. That is to say, the hydrol
of chromium sulphide is so considerable that the compound can
exist, but decomposes into the substances which are formed from
by the action of water.

At a red-heat anhydrous *chromium sulphide* is formed from
elements in the form of metal grey, very stable crystals

601. Chromic Acids. When any chromium compound is te
with strong bases or their carbonates, they absorb oxygen from
air and form salts of the divalent anion CrO_4''. The similarit
this formula to that of sulphanion is not only an external
the two anions are isomorphous, *i.e.* their salts with the same ca
have the same form and crystallise with one another in var
proportions.

Chromanion, CrO_4'', is of a pure and strongly yellow colour,
all the solutions of the chromates, therefore, exhibit this colour
solubility relations of the chromates agree closely with those o
sulphates. Thus, the alkali metals form soluble salts; of the alk
earth metals, barium forms an extremely difficultly soluble salt,
the others form increasingly more soluble salts. Of the chromat

heavy metals, that of lead must be called difficultly soluble ; this agrees with what we have in the case of lead sulphate.

602 **Potassium Chromate**, K_2CrO_4, is a salt which crystallises anhydrous rhombic crystals. It is prepared commercially by fusing naturally occurring chrome ironstone with potashes with access of From the aqueous solution it is usual to first prepare the better crystallising potassium dichromate (*vide infra*); from this the normal chromate can be obtained by adding the requisite quantity of potassium hydroxide or potassium carbonate

Potassium chromate is, at the ordinary temperatures, a sulphur-yellow salt ; on being heated it becomes of a bright red colour, but on cooling again assumes its yellow colour. We are here dealing with a shifting of the region in which the salt absorbs the rays of white light with the temperature, the region of the absorption shifting, with rise of temperature, from the violet (which gives the complementary colour yellow, cf. p. 12) towards the green—that is, towards the region of longer wave lengths.

The aqueous solution of potassium chromate exhibits an alkaline reaction. This is not due to the chromic acid being a weak acid in the true sense, but is due to the great tendency of the chromates to pass into salts of the condensed dichromic acid, whereby a process similar to hydrolysis is effected. For if any acid, even a weak one, is added to the solution of potassium chromate, a change of colour from yellow to orange occurs, and from the solution another potassium salt crystallises, the composition of which is represented by the formula $K_2Cr_2O_7$. It is therefore the potassium salt of the *condensed* anion, Cr_2O_7'', i.e. an anion formed from chromanion by the taking up of chromium trioxide. We have already met with such compounds in the case of sulphurous and sulphuric acids, which were distinguished as "pyro-acids" from the normal ones. The corresponding chromic acid, however, is not called pyrochromic acid but *dichromic acid*.

The transformation of chromanion into dichromanion takes place according to the equation $2CrO_4'' + 2H' = Cr_2O_7'' + H_2O$ For it, therefore, hydrion is necessary, and the reaction accordingly occurs on acidifying the chromates, which contain the ion CrO_4''. In the solutions of the normal chromates the hydrion of the water is used for this purpose; for this reason hydroxidion remains over and the solution reacts alkaline. The hydrolysis which occurs here differs from ordinary hydrolysis (p. 250) in the fact that in this case a condensed ion is formed and not a neutral compound.

For this reason, also, a solution of chromic acid, H_2CrO_4, cannot exist, since, indeed, the hydrion necessary for the transformation is present. When a concentrated solution of potassium dichromate is treated with excess of sulphuric acid, *chromium trioxide*, CrO_3, the anhydride of chromic and dichromic acid, separates out in long, red needle shaped crystals, which are readily soluble in water and

exhibit powerful oxidising actions. The aqueous solution of chromium trioxide does not have the bright yellow colour of chromanion or the orange colour of dichromanion, and its behaviour also with regard to the depression of the freezing point and electrical conductivity, allows only of the view that it contains the ions Cr_2O_7'' and H. If potassium dichromate is mixed with potassium hydroxide, the solution becomes bright yellow and contains potassium chromate. The following reaction occurs: $Cr_2O_7'' + 2OH = 2CrO_4'' - H_2O$. This is the reverse of the reaction just given, and occurs under the influence of hydroxidion. Dichromanion, therefore, cannot exist in measurable quantity in presence of hydroxidion, any more than chromanion in presence of hydrion.

At the present day chromium trioxide is placed at a cheap price on the market, since it is greatly used for galvanic cells and as an oxidising agent in the chemical industry, and since its ready solubility allows of more concentrated solutions of it being prepared than of potassium dichromate, which was formerly employed. Even on being heated it loses a part of its oxygen and passes into chromium oxide. The change takes place more easily in presence of acids, especially sulphuric acid, which form a corresponding chromic salt. This holds good also for the application of chromium trioxide as an oxidising agent. Hydrochloric acid evolves not oxygen but chlorine, being itself oxidised.

603. **Potassium Dichromate** is a red-coloured salt which reacts almost neutral; in its solution, therefore, the presence of an acid chromate is not to be assumed. It readily fuses to a dark liquid, which on cooling undergoes crystallisation and falls to a powder. It is moderately soluble in water (1 : 10, at room temperature); it crystallises anhydrous.

When potassium dichromate and sulphuric acid are used for oxidation purposes, chrome alum is formed: $K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O$

The corresponding sodium salts, *sodium chromate* and *sodium dichromate*, replace the potassium salts at the present time in their applications, since they can be manufactured more cheaply than the latter, by the fusion of chrome ironstone with soda (and lime to facilitate the reaction). The normal chromate crystallises with $10H_2O$ in the forms and possessing the general solubility relations of Glauber's salt (p. 490); the *dichromate* crystallises with $2H_2O$.

Of the other chromates, *barium chromate* may be mentioned. This is obtained as a bright yellow precipitate when the ions Ba and CrO_4'' come together in solution. The salt is very stable, withstanding a red heat without decomposition, and is therefore used as a reliable pigment for painting porcelain.

Barium dichromate is not known in the pure form, but its existence in solution can be gathered from the known facts. If the ion

and Cr_2O_7'' are brought together in solution, barium chromate and the corresponding salt is formed, and the solution becomes The precipitation is not complete, since, for example, if equivalent quantities of barium chloride and potassium dichromate are used, about half of the barium remains in solution, and the latter has the yellow colour of dichromanion. The cause of this is that in the solution of dichromate, chromanion is also present, being formed in small amount by the transformation of dichromanion into chromanion through the interaction with water: $Cr_2O_7'' + H_2O = 2CrO_4'' + 2H'$. This reaction is the reversal of that given on p. 615; it is a case of chemical equilibrium, none of the possible reactions complete, but at the end all the substances concerned in the equilibrium must be present. By precipitation as barium chromate chromanion is removed for the solution, a fresh amount is formed is also precipitated, and so on. That all the dichromanion does into chromanion is due to the fact that hydrion is produced same time, as the above equation shows. The amount of this as the reaction proceeds, the stability of the chromanion is diminished, that of the dichromanion is increased, and finally equilibrium must be established. In the solution dichromanion and exist side by side without being precipitated, which proves barium dichromate is a readily soluble compound. The cause of conversion of dichromanion into chromanion is, therefore, in the case, the difficult solubility of barium chromate. Since these evidently hold good universally, every cation that forms soluble chromate will precipitate this from solutions of chromates. This is, as a matter of fact, the case, e.g. lead

oxidising action of chromic acid can be made use of for its determination by employing it to liberate iodine from iodide, or, in other words, to convert iodation into iodine. action is

$$Cr_2O_7'' + 14H' + 6I' = 2Cr''' + 7H_2O + 3I_2$$
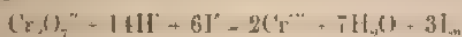
6 equivalents of some anion must be added to both sides to make the equation complete. From this it can be seen that amount of hydrion is used up in this reaction, which is possible, only in presence of much acid. For one combining weight three combining weights of iodine are set free; by means sulphate (p. 496) the amount of the latter can easily be determined

4. Sensitive Chromate Mixtures. Although the chromates are not to any great extent sensitive to light, they become a very high degree when they are in contact with reducing organic matter like paper, indiarubber, glue, etc. And sensitiveness is, strange to say, greater in the case of the dry than when these are moist. On this property a large number

of photographic and photo-mechanical methods depend, some of which may be mentioned here.

A mixture of glue and a soluble chromate on exposure to light acquires the property that the glue becomes *insoluble*. This is due to the fact that the chromic acid is reduced to chromium oxide, which forms an insoluble compound with the glue (p. 612). If some colouring matter is added to the above mixture, and paper is coated with this and exposed to light under a transparent picture, the glue becomes insoluble at those parts on which the light has been allowed to act, while it remains soluble at the parts where the opaque parts of the picture were. If the prepared paper is treated, after the exposure, with warm water the coating is dissolved at those parts which were protected from the action of light, while the colour remains at the exposed parts. In order to obtain a picture, therefore, in its proper relations, a "negative" must be used, *i.e.* a transparent picture in which the dark parts are transparent and the bright parts opaque. Such pictures are obtained by the ordinary photographic methods of silver salts (Chap. XXXV.)

Another method depends on the fact that a mixture of glue and chromate acquires at the exposed parts the property of taking the *non-printing colour*, while the non-exposed portions (after the treatment with water) are not coloured by this. If, therefore, the printing colour is rolled over such a picture and a white paper placed on it, a print is obtained in which the exposed parts are again dark and the unexposed bright.

If a metal plate is coated with the chromate-glue mixture, and the part remaining soluble after exposure removed with warm water, the exposed metal can be deeply etched by pouring acid on it. In this way blocks for printing are obtained.

These examples do not exhaust the whole of the possibilities, but we must refrain from further details.

605. Chromyl Chloride and Chlorochromic Acid. The similarity of chromic acid to sulphuric acid is further exhibited by the fact that it can form the two chlorides which can be derived from the acid by the replacement of hydroxyl by chlorine.

By distilling a mixture of potassium dichromate and sodium chloride with sulphuric acid, *chromyl chloride*, CrO_2Cl_2, is formed as a red liquid similar to bromine, which boils at 118°, and has an appreciable vapour pressure even at the ordinary temperature. As the substance is sensitive to water, the water formed in the reaction must be bound using acid containing anhydride, or fuming acid.

Chromyl chloride decomposes, after the manner of the acid chlorides, into chromic acid and hydrogen chloride :

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$
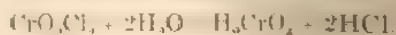
The process is, however, half reversible, since, in concentrated

idation, chromic acid and hydrochloric acid undergo partial combination, with formation of the corresponding first chloride of chromic acid. This is not known in the free state, but salts of chlorochromanion are known. The state of affairs is therefore exactly the reverse of that obtaining in the case of sulphuric acid, where the free acid is known but not the salts. Potassium chlorochromate, $KCrO_3Cl$, is obtained as an orange, anhydrous salt by crystallising potassium dichromate from a strong solution of hydrochloric acid: $K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$. On recrystallising from pure water, it again decomposes into hydrochloric acid and potassium dichromate. On being heated it evolves chlorine.

* The formation of chromyl chloride is used for the detection of chlorine in presence of bromidion and iodidion. On distilling the salts in question with potassium dichromate and fuming sulphuric acid chlorine passes over as chromyl chloride, while bromine and iodine distil over in the free state. The distillate is treated with ammonia, whereby chromyl chloride yields a yellow solution of ammonium chromate, while bromine and iodine dissolve to a colourless solution.

A *chromyl fluoride*, CrO_2F_2, a red, very volatile liquid, is also known similarly to the chloride, it is obtained by the distillation of a chromate with fluor spar and fuming sulphuric acid. It is very rapidly decomposed by water.

606 **Perchromic Acid.** —By this name a higher stage of oxidation of chromium is designated, which is formed by the action of *hydrogen peroxide* on an acid solution of dichromic acid. The solution at once becomes *blue*; the coloration, however, is not stable, for in a short time oxygen is evolved and a chromic salt is left in the solution. The phenomenon can be made to last longer by shaking out the blue liquid with ether; the blue substance then passes into the ether, in which it keeps much longer.

The composition of this blue compound has, it is true, been determined, but the relations which are met with in this reaction have not been sufficiently explained in order to be treated here.

Since the blue coloration becomes visible with even very small quantities of hydrogen peroxide, an acidified solution of a chromate can be used as a reagent for hydrogen peroxide.

CHAPTER XXX

COBALT AND NICKEL

607. **Cobalt** and **nickel** are two metals allied to iron, and similar to it as far as the compounds of the ferrous series are concerned, but the compounds corresponding to the ferric series are unstable or unknown. These metals, further, share with iron the property of being markedly *magnetic*, and they also accompany iron in meteorites. Their occurrence in nature is not exactly rare, but they are much more sparingly distributed than iron. They occur chiefly as constituents of complex sulphur and arsenic compounds, and from these they are obtained by first of all being freed from the sulphur and arsenic by roasting, or exposure to the oxidising action of the air at a high temperature, whereby they pass into the respective oxides. These oxides are separated from one another in the wet way by the fractional precipitation of the salts prepared from them.

The two elements are grey or yellowish-white metals, the melting point of which is very high, although lower than that of pure iron. They are hard and tenacious metals, which take on a very fine polish; they remain almost unchanged in the air, and have a fairly considerable technical value.

The two elements form divalent, elementary ions; further, they have a great tendency to form complex ions of all kinds. In the case of cobalt, more especially, an extraordinary wealth of different compounds exists, these being chiefly compounds with nitrogen in its various forms of combination, cyanogen, ammonia, and the oxygen compounds.

The combining weights of these elements have been determined by the analysis of their halogen compounds, and have been found to be $Co = 59.0$, $Ni = 58.7$.

608. **Metallic Cobalt** can be easily obtained as a powder by heating the oxide in a current of hydrogen. In fused masses it is most easily obtained by reduction with aluminium, according to the method of Goldschmidt. It is a tenacious metal, which can be readily polished, and which exhibits a high lustre. In the metallic state it has as yet found no application in the arts.

In most acids it dissolves only very slowly, with evolution of hydrogen, but dissolves readily in nitric acid. The solutions which are formed are coloured red, irrespective of the nature of the acid ; it is to be concluded from this that the red colour is due to *cobaltion*. The cobaltion, Co , contained in the salts is divalent, and in its general behaviour is similar to ihferrion

With alkalis, its salts yield a blue-violet precipitate of *cobalt hydroxide*, $Co(OH)_2$, which is converted into its anhydride, green *cobaltous oxide*, CoO, on being heated out of contact with oxygen. At a red heat it takes up oxygen from the air, and an *oxide*, Co_3O_4, corresponding to magnetic iron ore, is formed, which is again converted into the monoxide at a white-heat

Cobalt hydroxide does not dissolve in excess of alkalis (except in traces, when the solutions are very concentrated), but readily does so in solutions of ammonium salts. The reaction is, in the first instance, similar to that in the case of magnesium hydroxide ; but if a large excess of ammonia is added, the red colour changes to a yellow-brown, which shows that a new, complex compound has been formed. If the liquid is diluted with much water, blue cobalt hydroxide separates out as a flocculent precipitate. As in the case of manganese, the ammoniacal solution absorbs oxygen from the air, whereby complex salts are formed which will be mentioned later.

Of the salts of cobalt, cobalt nitrate, $(CoNO_3)_2$, is the best known ; this is a readily soluble salt crystallising with $6H_2O$, and is used in analytical chemistry.

609. Cobalt Chloride, $CoCl_2 . 6H_2O$, is also readily soluble. It forms a large number of lower hydrates, of which the less hydrated forms are of a blue colour. The concentrated aqueous solutions, also, which are red in the cold, exhibit a blue colour when heated. This occurs still more readily when the solution contains a large amount of chloridion in the form of sodium chloride or hydrochloric acid. The cause of this is that under these circumstances complex anions are formed probably by the taking up of chloridion by cobalt chloride, which are blue in colour.

' This phenomenon was formerly regarded as a great curiosity, and cobalt chloride was used as a "sympathetic ink." For, on writing on paper with a solution of this salt, the pale red tracings are scarcely recognisable in the ordinary state. On heating the paper, however, and thereby converting the salt into the less hydrated form, the blue colour appears very distinctly.

' Textile material moistened with a concentrated solution of the salt, assumes various colours when exposed to the air, according to the amount of moisture in the latter. In dry air it is blue ; in moist, pale red ; in the intermediate states, violet colours appear. Such material is used as a rough hygroscope, because, from its colour, an idea can be obtained of the amount of moisture in the air and the probability of rain.

The ... ...ical composition of ...
cobalt ... ...ins three to six ...
salts. T... ...ormulæ, therefore, ...
$Co...$ ... ...ould be $CoCl... ...NH...$
ferrou... ... ., however, do not ...
forms, ... very stable and d... ...
tion, ...cial reactions which ...
and ... ...re, therefore, salts of ...
type ... ...s of ammonia. They ...
... ...d as compounds of ... ...
pound ... $...o(NH_3)_n$... In oppos... ...
cob... ...., also, which are cont... ...
imp... ... ...reactions of these ions, ...
pho... ... ...e that the elements of ...
bl... ... ...mplex cation.
N... ... ...s a survey of the vari... ...
d... ... ... these compounds is ...
p... ... ...vident. The compounds ...
... ...ble anions are united ...
... ...stable anions appear ...
... ... ammonia. To this the ...
... ...re never more than three ...
... ...ssely with one mole... ...
... ...
                              $NH... ...$
                              $N... ...$
                              $... ...$
                              $... ...$

ken here, especially as many problems regarding their nature still remain unsolved. We shall merely state generally that the complex cations of these salts are almost all more or less brightly coloured: the old designation of these salts, indeed, is derived from their colorations. The "*luteocobaltic*" salts are the compounds of the first type, the *purpureo*-salts belong to the second, the *praseo*-, *flavo*- and *croceo*-salts to the third type. The complex cations mostly form strong bases with hydroxyl, which are soluble in water and exhibit the reactions of hydroxidion in a most pronounced manner. Their salts are frequently very difficultly soluble in water.

615. **Nickel.**—Unlike cobalt, which is not employed in the metallic state, *metallic nickel* is a material which is greatly used. It was formerly used only for alloys; thus *German silver* is an alloy of nickel with zinc and copper. Some decades ago, however, the difficulties caused by the high temperature of fusion of nickel have been overcome (especially since it was found that it could be rendered more easily fusible by the addition of metallic magnesium or aluminium), and at the present day nickel is extensively employed in cases where it is required to use a tenacious and hard metal, and one which keeps well in the air and is difficultly fusible. It finds increasing use, therefore, for apparatus in the laboratory and for household utensils.

Further, large quantities of nickel are deposited on other metals with the help of the electric current. It coats these with a resistant, almost silver-white layer, which keeps well in moist air, so that the *nickel-plating* of various objects made of iron and brass has become an extensive industry.

' The electrical deposition of a metal depends on the fact that at the cathode of a circuit, the cations pass from the state of ions into the neutral state. In the case of nickelion, this passes into metallic nickel, which is deposited at all points where the current leaves the liquid In this process various circumstances, such as strength of the current, nature of the solution, etc., have a considerable influence on whether the metal is deposited in a coherent, lustrous layer or as an incoherent powder. The practice of *electro-plating*, as this process is called, depends on the knowledge and application of the conditions which ensure the formation of a good deposit. This subject, which is very important in the arts, has been only very little investigated scientifically, so that no general rules can be given.

' In order that the nickel-plating bath, which constantly gives up metal to the object to be plated, may not become exhausted, the anode is made of metallic nickel. By this means the anion is not discharged, but on the contrary, as much neutral or metallic nickel passes into the ionic state as is separated at the cathode and the whole process consists metal passing into ions at the anode, and being transported by the current to the cathode, where it again passes from the ionic state into the metallic. In this process the current would, theoretically,

2 s

have practically no work to perform ; as a matter of fact, however, a larger or smaller amount of work must be performed by the current on account of the differences in the concentration and other circumstances, a fact which finds expression in the so-called *polarisation* of the bath or the "bath potential."

Nickel forms a divalent elementary ion, *nickelion*, Ni``, which is of a fine green colour ; this colour is present in all solutions of nickel salts which contain this ion. Nickel, it is true, can also form a higher stage of oxidation, but this is extremely unstable, and does not behave as a salt-forming oxide. Nickel can form complex ions, but these are neither so varied nor so stable as in the case of cobalt ; this forms the most essential difference between the otherwise very similar elements.

Nickel salts are obtained by the solution of metallic nickel in an acid ; in the case of nickel, the decomposition of aqueous acid solutions with evolution of hydrogen takes place only very feebly and slowly. If *aqua regia* is employed, the chloride is obtained ; by evaporating the nitrate with sulphuric acid, the former is converted into the sulphate.

From the green solutions of the nickel salts, soluble bases give a pale green precipitate of *nickel hydroxide*, $Ni(OH)_2$, which loses water when heated, and is converted into grey *nickel oxide*, NiO. Nickel hydroxide is not soluble in alkalis, but dissolves in ammonia. As the liquid thereby becomes of an azure blue colour, it must be concluded that a new ion is formed. The investigation of the solid salts has shown that we are possibly dealing with two different ions, one of which contains $4NH_3$, the other $6NH_3$, to one Ni ; the ions, therefore, have the formulæ $Ni(NH_3)_4$`` and $Ni(NH_3)_6$``. They are both blue.*

* The complex ions of nickel containing ammonia differ from those of cobalt, not only in being derived from divalent nickel, but also in being much less stable. Whereas most of the cobalt-ammonia compounds can be brought together with bases, and even in some cases boiled with them, without ammonia being eliminated to any appreciable extent, the salts of the nickel-ammonia ions in the solid state slowly lose their ammonia even in the air, and quickly on heating. The dissociation pressure of these compounds therefore in respect of the ammonia has an appreciable value even at the ordinary temperature, while in the case of the cobalt compounds it is immeasurably small.

The nickel salts are similar to those of cobalt and generally isomorphous with them. Of these salts some importance is possessed by *nickel sulphate*, which is generally obtained in quadratic crystals with $6H_2O$, a form which is seldom found in the case of the other vitriols ; it can, however, also crystallise in the forms of magnesium sulphate and ferrous sulphate. With potassium and ammonium sulphate it forms double salts of the oft-mentioned type. Nickel sulphate and double salt with ammonium sulphate are used in large quantities for the preparation of baths for nickel-plating.

With potassium cyanide, the nickel salts at first deposit a green precipitate of *nickelous cyanide*, which dissolves in excess of potassium cyanide and yields a *yellow* liquid. From this change of colour it can be seen that a new ion is produced; on evaporating the solution a yellow salt of the composition $K_2Ni(CN)_4 . H_2O$ crystallises out. The combination which forms the basis of this salt does not have an analogous composition to the complex ions of iron, manganese, and cobalt, but it is only divalent. With regard to its stability, also, it differs greatly from these compounds. On acidifying the solution one does not obtain free hydronickelcyanic acid, but a greenish precipitate of nickelous cyanide is produced and hydrocyanic acid escapes. The acid, therefore, immediately decomposes according to the equation $Ni(CN)_4 - Ni(CN)_2 + 2HCN$. A separation of cobalt and nickel can be based on this reaction.

616. Nickel Carbonyl.—If carbon monoxide is kept in contact with finely divided nickel at a temperature of about 30°, the two substances combine to form a colourless liquid which boils at as low as 43°, and has an unpleasant smell and poisonous action. The composition and vapour density are represented by the formula $Ni(CO)_4$.

The liquid is not appreciably soluble in water, but it readily dissolves in organic liquids, such as benzene and turpentine. In the air it oxidises to substances of complex composition.

At a somewhat higher temperature, nickel carbonyl again decomposes into its constituents; for each temperature there exists a relation between the carbon monoxide and the vaporous nickel carbonyl at which equilibrium exists with metallic nickel: with rising temperature the equilibrium shifts in favour of the carbon monoxide.

By reason of this, nickel can be separated in the pure state from ores after it has been reduced to spongy metal at a low temperature. When monoxide is passed over it, and the resulting gas mixture is heated, metallic nickel is thereby deposited and the liberated carbon monoxide can be used for the conversion of fresh quantities of nickel. For technical purposes, however, this process cannot be employed, because, under the above conditions, the carbon monoxide also undergoes decomposition into carbon and carbon dioxide, $2CO - C + CO_2$, which disturbs the cycle of processes.

The change of equilibrium with rise of temperature brings it about that metallic nickel can be distilled from a lower to a higher temperature. Carbon monoxide is enclosed in a glass tube, at one end of which there is nickel sponge; the end at which the nickel is not placed is heated to 100° or somewhat over this. After a short time the hot end becomes covered with a fine mirror of metallic nickel.

ZINC AND CADMIUM

417. Zinc.—Among the metals of the iron group, to which in many respects similar, zinc differs in the fact that it catches fire at a rather stage of combination than that containing trivalent iron, respect it forms an intermediate member between iron, which has lost this property for the most part, and magnesium, in the case of which no trace of that property is present.

Zinc occurs fairly abundantly in nature, both as oxide, as carbonate and silicate, and as sulphide or blende. Zinc is obtained from both these and is a white, fairly soft metal which melts at 420 and boils at 950. In the air and in water it oxidises quickly. Since however, the zinc hydroxide or carbonate so formed covers the underlying metal with a coherent coating, oxidation proceeds for the most part slowly, and objects of zinc resist the influences of air and water fairly well.

Cast zinc is coarsely crystalline and brittle. If, however, the metal is heated to somewhat over 100, it becomes soft and tough, and can be hammered and rolled. Having once undergone the treatment, it remains tenacious even at the ordinary temperature. If heated to about 300, it again becomes extremely brittle, and at this temperature can be ground to a powder; on being cooled, it retains somewhat brittle character.

Zinc is employed not only in the pure state, but also to a considerable extent in *alloys*. Its most important alloy is that with copper, called *brass*, and will be treated under copper. With copper and nickel it forms *German silver* (p. 625).

Zinc is also used for coating iron in order to protect it from rust; this is then known as "galvanised" iron. Iron objects which are constantly exposed to the air, such as railings, agricultural implements etc., are in this way rendered durable. It is true that zinc in contact with iron oxidises more quickly than when alone, but the oxidation is limited to the surface.

At 420 zinc fuses, and this temperature is low enough to allow

e metal being largely used for castings.   At 950° zinc is converted
to a vapour, which burns in the air with a brilliant blue flame, forming
the oxide.   The density of this vapour yields the molar weight 65 1 :
this number also represents the combining weight, the formula of zinc
in the vaporous state is Zn.   It contains, therefore, only one combining
weight, whereas most of the elements in the gaseous or vaporous form
have the double formula.   The other metals, however, so far as they
are known in the vaporous state, exhibit the same peculiarity as zinc.

It is on the volatility of zinc that its manufacture depends.   The
oxygen ores are heated directly with charcoal ; the sulphide, after
being converted into zinc oxide by roasting in the air.   The metal formed
by the reduction of the oxide with charcoal volatilises and is collected
in suitable receivers with exclusion of air, while the impurities remain
behind in the retort.

In this process a portion of the metal is obtained in a form in
which it is often used in the laboratory, viz. as zinc dust.   So long as
the temperature of the receiver remains below the melting-point of
zinc, the metal is deposited in the form of a fine grey powder.   (The
relations are exactly the same as in the formation of flowers of
sulphur.)   This powdery form of zinc is more suitable for many
chemical purposes than the fused ; in using it, however, it must be
remembered that it generally contains a considerable amount of zinc
oxide in consequence of an incipient oxidation.

Recently many attempts have been made to obtain zinc from its
ores by first converting it into a salt and then decomposing this by
means of the electric current.   The difficulty of obtaining a coherent
metal free from oxide in this way does not appear as yet to have been
overcome.

614. Zincion.—Metallic zinc readily dissolves in acids with
evolution of hydrogen (p. 187), and is converted into the corresponding
salt, *zincion*, Zn··, being formed from the metal.

Zincion is divalent, and resembles magnesium in many respects.
Like the latter it is colourless, and with the different anions it forms
salts which have similar solubilities and the same crystalline forms as
the magnesium salts.   Zincion is a poison for the higher organisms ;
nevertheless, it has been found as a constituent of some plants which
grow in soil containing zinc.

The heat of formation of zincion from the metal is 147 kj.   This
is, therefore, also the amount of heat developed by the solution of
zinc in acids (p. 204).

During the dissolution some remarkable peculiarities are observed.
Pure zinc appears as almost insoluble in dilute acids   So soon, how-
ever, as there is added a small quantity of a salt of copper, silver, lead,
or some other metal, which is eliminated from its solutions by zinc, a
rapid evolution of hydrogen at once occurs.   The cause of this is at
once seen on touching a piece of zinc immersed in an acid with a piece

of another metal. Hydrogen is abundantly evolved, but only at the surface of the other metal, while the zinc passes quietly into solution. If different metals are used as cathodes for an electrical current in dilute acid, it is seen that for the evolution of hydrogen at a surface of zinc a much higher potential is required than in the case of any other metal.

* The process may therefore be pictured as if the zinc withdrew the charge from the hydrion, passing thereby into zincion, while the hydrogen assumes the gaseous form. This passage into the gaseous state takes place (for reasons which are not yet known, but which are detected by the potential) with much greater difficulty at a surface of zinc than at the surface of another metal, and for this reason the decomposition is slight so long as only zinc surfaces are available for the evolution of gas. If, however, the zinc is connected by a conductor with another metal at the surface of which the hydrogen can be more
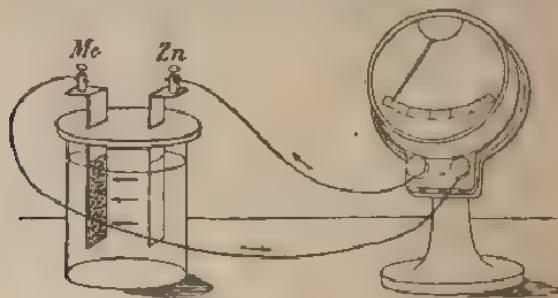
Fig. 117.

readily evolved, the formation of the zincion and the elimination of the hydrogen take place at different points, an electric current passing at the same time through the metals and the acid. In Fig. 117 a clear picture of these relations is given. From the zinc, denoted by Zn the metal dissolves as ion; the requisite amounts of positive electricity are withdrawn from the hydrion present in the solution, these charges passing in the direction of the arrows through the metallic conductor to the zinc. The simultaneous production of an electric current is therefore, the necessary condition for the dissolution of zinc and the evolution of hydrogen occurring at two different points.

* The above arrangement affords at the same time an insight into the production of electric currents in the old voltaic cell, consisting of zinc, copper, and dilute acid. Fuller information on this point will be given at a later point (Chap. XXXII.).

619. Zinc Hydroxide, $Zn(OH)_2$, is deposited as a white, flocculent precipitate on the addition of dissolved bases to a solution containing zincion. It is soluble in an excess both of alkali and of ammonia, although for different reasons in the two cases. The solubility in

alkali depends on its property of splitting off hydrion from its hydroxyl, and therefore of acting as an acid. These solutions contain an alkali oxide, e.g. K_2ZnO_2, and the new ions ZnO_2 and $HZnO_2'$. The reason of the solubility is therefore the same as in the case of alumina (p. 560). The solubility of zinc hydroxide in ammonia, however, depends on other causes. We might regard it as being due to an influence exerted on the solubility by the presence of ammonion, such as occurs in the case of the otherwise very similar magnesia (p. 541) This appears, however, to be excluded from the fact that zinc hydroxide must be a much weaker base, as is evident from its solubility in alkalis (p. 560). On the contrary, we have here to assume the formation of new ammonium ions, $Zn(NH_3)_n$, where n has presumably several values. The behaviour of zinc hydroxide is therefore comparable with that of nickel hydroxide, in which case the formation of new ions was rendered visible by the change of colour.

* This assumption is supported by the fact that the zinc salts, especially the halogen compounds, even when dry, readily combine with ammonia without undergoing decomposition.

On being heated, zinc hydroxide loses water, and is converted into white zinc oxide, ZnO. The same compound is obtained by heating metallic zinc in the air; in this way it is prepared on the large scale for use as a pigment under the name zinc white.

Over white lead, which is employed for similar purposes, zinc white has the advantage of being less poisonous, and of remaining white even in an atmosphere containing sulphuretted hydrogen, whereas the former becomes dark in colour. White-lead, however, has a better covering power, since it has a considerably higher coefficient of refraction than zinc white, and for this reason it is still often preferred.

* The use of colourless substances, as white paints, depends on the fact that in the small particles of which the paint consists the light undergoes repeated refraction, and is ultimately totally reflected. This total reflection effects the "covering" power, i.e. the opacity of the layer Of the variously directed rays in an opaque body, the number of those which are totally reflected is all the greater, the greater the index of refraction, because the angle at which the light rays can still pass through decreases in the same proportion Hence proportionately thin layers suffice in order to reflect all the incident light.

Zinc oxide is white in the cold, but appears yellow when hot; on cooling it again acquires a white colour. This colour change must not be regarded as a sign of the conversion of the zinc oxide into another, perhaps allotropic, condition, for it does not take place suddenly, as in such a case it would do, but gradually. It is solely due to the fact that the region in which zinc oxide absorbs rays moves, on heating, from the ultra-violet portion of the spectrum, in which it is situated at the ordinary temperature, towards the visible violet portion. This is a very general phenomenon, viz. that the region of absorption of rays

changes in the above sense with the temperature. White substances
become yellow on being heated, yellow ones red (p. 615), and red ones
brown; blue and green substances, on the other hand, generally undergo
no marked change of colour on heating. Conversely, yellow and red
substances (with the exception of organic dyes) become more pale, or
even colourless, on being cooled, say in liquid air.

620. **Zinc Chloride**, $ZnCl_2$, is a white, readily soluble salt, which
boils as low as 730, and can be easily obtained in the dry or wet way
by the action of hydrochloric acid on zinc or zinc oxide. On being
evaporated to dryness, the aqueous solution loses hydrochloric acid.
The product can be again freed from oxygen by distillation in a current
of hydrogen chloride or by the electrolysis of the fused salt, the spongy
zinc which separates out acting as a purifying agent. Zinc chloride
melts very readily to a clear, strongly refracting liquid.

Zinc chloride is used as a preventive of the destruction of wood by
micro-organisms and fungi, e.g. in the case of railway sleepers. Further,
it is used as a flux for soft solder. In this case its action is due to its
power of dissolving metallic oxides (p. 435).

A concentrated solution of zinc chloride dissolves large quantities
of zinc oxide. From the solution an oxychloride, $Zn\begin{smallmatrix}OH\\Cl\end{smallmatrix}$, crystallises
out. If the solution is very concentrated, the whole solidifies to a
hard mass of oxychloride. This phenomenon is made use of for the
preparation of a cement, a solution of zinc chloride of syrupy consist-
ency being rubbed together with zinc oxide shortly before it is required
for use.

On diluting the solution containing the oxychloride with water,
that substance (or, in the case of very dilute solutions, zinc hydroxide)
is precipitated. Since almost all commercial zinc chloride contains
oxychloride, i.e. has lost hydrogen chloride on evaporation to dryness,
the same phenomenon is there met with, the salt yielding a turbid
solution, or, on dilution, depositing a white precipitate.

The formation of a basic precipitate is also promoted by the hydro-
lytic decomposition of the zinc chloride in the solution. On account
of the feebly basic properties of the hydroxide, this decomposition is
rather considerable, and manifests itself in the acid reaction exhibited
by the solutions of all zinc salts.

621. **Zinc Sulphate**, or zinc vitriol, $ZnSO_4$, generally crystallises
with $7H_2O$ in the rhombic forms of magnesium sulphate. According
to the temperature, however, it can crystallise with other amounts of
water, and in other forms. It is a colourless salt, very readily soluble
in water, and can be obtained by the action of sulphuric acid on zinc
oxide or metallic zinc; it is employed in the arts and in medicine. It
forms, with the sulphates of potassium and ammonium, double salts,
containing $6H_2O$.

622. **Zinc Carbonate**, $ZnCO_3$, occurs naturally as *calamine*, and

a highly valued zinc ore. It crystallises in rhombohedra, which are isomorphous with those of calc-spar. As in the case of magnesia, *basic carbonates*, varying with the temperature and the dilution, are mostly obtained by precipitating aqueous solutions of zinc salts with alkali carbonates. They are converted into zinc oxide by ignition. Precipitation as carbonate, and weighing as oxide, are used for the analytical determination of zinc.

623. **Zinc Silicate** also occurs naturally as *siliceous calamine*. It is also used in the manufacture of zinc.

624. **Zinc Sulphide,** ZnS, is obtained as a white, hydrated precipitate by the addition of ammonium sulphide to zinc salts. Of the better known heavy metals zinc is the only one which forms a white sulphide ; this serves as a convenient characteristic in analysis. Zinc sulphide is soluble in dilute acids with liberation of sulphuretted hydrogen. The reaction takes place in a manner similar to that in the case of iron sulphide (p. 586), but with the difference that zinc sulphide is considerably less soluble. This is the reason that a *neutral* solution of zinc sulphate or zinc chloride is precipitated by sulphuretted hydrogen ; not until a pretty considerable portion of the salt has undergone double decomposition does the concentration of the hydrion produced reach such a value as to hinder further precipitation. If the concentration of the hydrion is raised to this value to start with, by the addition of hydrochloric or sulphuric acid, no precipitation is produced by sulphuretted hydrogen. For equilibrium depends only on the relative concentrations existing in the solution, and not on the amount of the solid substances.

If, however, by suitable means the concentration of the hydrion is kept so low that the state of equilibrium is not reached, the zinc can be almost completely precipitated from acid solutions. As has been mentioned several times, this is brought about by the addition of an *acetate*. The acetanion present then withdraws the hydrion produced in order to form undissociated acetic acid, and only a very small portion of the hydrion escapes this combination.

If in this manner zinc is precipitated from acetic acid solution in presence of cobalt and nickel, white zinc sulphide is first deposited, and black cobalt sulphide and nickel sulphide do not make their appearance till later. In this way the presence of zinc along with those other metals can be detected in analysis.

In nature, zinc sulphide occurs in brown to black masses, and is called *zinc blende*, or simply *blende*. It is an important zinc ore. The sulphur is removed by roasting, and the oxide formed is reduced with charcoal. The process which occurs in the roasting is represented by the equation $2ZnS + 3O_2 = 2ZnO + 2SO_2$. The sulphur dioxide thereby produced is used for the preparation of sulphuric acid. This is done not only for the sake of utilising it, but also in order that it may not escape into the air and exert its destructive action on plant growth.

625. Cadmium.—This element, which is very similar to zinc occurs in comparatively small amount in nature, associated with that metal.   As it is more readily volatile than zinc, it collects in the first portions of the distillate in the preparation of the latter   It is a bluish white metal, almost as soft as lead ; it melts at 320   and boils at 770 Its vapour density points to a molar weight, which is equal to the combining weight, Cd = 112·4 ;   the formula of the element in the vaporous state is therefore Cd, similarly to zinc.

Cadmium forms only one elementary ion, divalent cadmium, Cd The metal dissolves, although very slowly, in aqueous acids with form tion of this ion.   Cadmion is colourless, and acts as a rather violent poison on the lower and higher organisms.   Its heat of formation from the metal is 77 kj.

The cadmium salts in aqueous solution are distinguished by the fact that many of them are considerably less dissociated into ions than the corresponding salts of the other divalent cations.   This is especially noticeable in the case of the halogen compounds.

From the aqueous solutions of the cadmium salts alkali hydroxide precipitate white *cadmium hydroxide*, which is insoluble in an excess of the precipitant.   This is in agreement with the general increase of the basic properties with increasing combining weight in the case of such elements.   Cadmium hydroxide is soluble in excess of ammonia.   The solution contains complex cadmium-ammonia ions, $Cd(NH_3)_6$..

By heating the hydroxide, and by the combustion of the metal in the air, *cadmium oxide* is obtained as a brown powder, which readily dissolves in acids to form cadmium salts

Of the salts the *sulphate* should be mentioned.   This still exhibit some similarity to the sulphates of the magnesium series, but also considerable divergence.   Thus, it crystallises at the ordinary temper ture in accordance with the formula $3(CdSO_4)$. $8H_2O$, for which there is no analogy known in the case of the true " vitriols."   The formation also of the typical double salt with potassium or ammonium sulphate does not take place quite readily.

The sulphate is readily soluble in water ; in the case of the salt with $\frac{7}{3}$rds molecules of water of crystallisation the temperature ha very little influence on the solubility.   It is used in medicine, and is also employed for the construction of electrical " standard cells."

The *halogen compounds* of cadmium exhibit especially clearly the above-mentioned slight dissociation in aqueous solution   Of the three compounds, *cadmium chloride* is most, *cadmium iodide* least, dissociated The latter salt forms crystalline laminæ of a pearly lustre, which are soluble in alcohol.   On account of this property it is employed in photography as an iodising salt.

* Apart from the small conductivity, the following experiment demonstrates very clearly the slight degree of dissociation of cadmium iodide.   If cadmium hydroxide is brought together with water and

litmus or phenolphthalein, no alkaline reaction can be detected, because the hydroxide is too slightly soluble. The same thing is observed on using a solution of potassium nitrate or sulphate instead of water. If we take a neutral solution of potassium *iodide*, however, a strong alkaline reaction is obtained on shaking up. The reason of this is that the cadmium which passes into solution from the hydroxide is converted into undissociated cadmium iodide. A fresh quantity of hydroxide must therefore pass into solution, and this must go on till equilibrium is attained. In this process the hydroxidion of the hydroxide remains over (along with potassium from the potassium iodide), and the solution must exhibit the reaction of hydroxidion, *i.e.* must react alkaline. In formulæ we have $Cd_2(OH)_2 + 2I' \rightleftharpoons CdI_2 + 2OH'$.

626 Cadmium Sulphide, CdS, is obtained as a fine yellow precipitate on passing sulphuretted hydrogen into a neutral solution of a cadmium salt. If the solution is acidified, precipitation occurs nevertheless, and a very considerable amount of acid must be added before sulphuretted hydrogen ceases to produce a precipitate. Similar chemical equilibria are obtained to those described in the case of zinc sulphide (p. 633), with this difference, however, that the concentration of hydrion necessary for equilibrium must be very much greater than in the case of zinc.

If we have a solution in which cadmium sulphide has just been formed, and we add potassium iodide (or any salt containing iodidion), the cadmium sulphide immediately passes into solution. The reason of this is again that owing to the formation of undissociated cadmium iodide, cadmion disappears from the solution, and must be replaced by the dissolution of a fresh portion of the precipitate.

On account of its pure yellow colour, cadmium sulphide is used in painting under the simple name "cadmium," since other cadmium compounds are not employed as pigments.

An amalgam of cadmium and mercury is employed by dentists as a filling for teeth, because it possesses the property of being soft and easily moulded for a short time after being prepared, but of very soon solidifying to a coherent, hard mass. This depends on the fact that the compound of the two metals is a crystalline substance, which is hard at the ordinary temperature, but which can be easily supercooled. In the soft mass, therefore, we have a superfused amalgam. When crystallisation has commenced it proceeds slowly through the whole mass, which thereby becomes hard.

CHAPTER XXXII

COPPER

627. General.—Between the metals of the new group, which is called after copper, and those of the former groups, many points of relationship exist. The circumstance that most of the heavy metals can form several series of compounds, *i.e.* ions of different valency, causes a crossing and interweaving of these mutual relationships which render it impossible to draw up a simple list of the elements in such a way that the most nearly related always stand together. For, indeed, on following out one of the existing series, other ones must be interrupted; for the sum of these mutual relationships cannot be represented by means of a straight line, but only as a much branched river system, or still better perhaps, as an arterial system exhibiting manifold anastomosis.

Thus in copper we have, on the one hand, a metal which in certain compounds shows itself to be related to the elements of the magnesium and iron series, while other compounds exhibit close relationships to silver and mercury. We have already frequently met with such ambiguity of behaviour, *e.g.* in the case of iron, and especially of manganese; it points to the fact that a systematisation of the chemical elements according to a single scheme is impossible, for a really exhaustive system must necessarily contain all the existing relationships, and must, therefore, be of such a form that these diversities receive adequate expression. The satisfactory solution of this problem has not as yet been attained, and we must at the present time get over the difficulty by pointing out, when necessary, the various relationships existing.

628. Copper.—Of the heavy metals already discussed, copper is the first that is found in any considerable quantity in the metallic state on the earth, and it belongs, therefore, together with silver and gold, to the metallic elements which have been longest known. It is distinguished from all other metals by its bright-red colour, which, however, is seen only on fresh surfaces. Even in a very short time these become covered with a dark coating of oxygen or sulphur com-

which, although it does not destroy the metallic lustre, changes
red colour of the pure metal into the brown-red, which is
alled copper red.

er melts at 1050°, has the density 8·9, and is, at the ordinary
ure, a tenacious metal which can be mechanically moulded,
h resists well the influences of the atmosphere and of moisture.
; exposed for a lengthened period to moist air, it is true, it
covered with a layer of oxygen compounds; this, however,
very thin, and effectually protects the metal underneath.   At
t copper combines fairly rapidly with oxygen to form a black,
ride, which readily breaks off in scales and exposes the under-
tal to fresh attack.

ccount of its chemical resistibility, its good mechanical proper-
its melting point, copper is largely employed for utensils of
.   Another very extended sphere of application of copper
on its great *conductivity for the electric current*.   In this
it is superior to all other accessible metals (silver is alone
to it), and very large quantities of it are therefore employed
o-technics.   For this purpose it must be very pure, since the
rity is greatly lowered even by very small amounts of foreign

les being used in the pure state, copper is also extensively
l for alloys.   Brass has already been mentioned, others will
later.

combining weight of copper is $Cu = 63·6$.

The Ions of Copper.—Copper forms two kinds of elemen-
, the monovalent monocuprion, Cu·, and the divalent dicuprion,
he latter is allied to the divalent ions previously described,
er belongs to a new type.   Of the two, the divalent one is by
nost frequent and better known, and, for that reason, shall be
ribed.

formation of *dicuprion* from metallic copper does not take
arly so readily as that of the ions of the metals hitherto
l.   Without the co-operation of the atmospheric oxygen,
ids have no appreciable action on metallic copper, and only
id or hot concentrated sulphuric acid have a solvent action.
not hydrogen but a reduction product of the particular acid
ed.   On the other hand, hydrogen gas acts on solutions of
alts, eliminating copper from them with the simultaneous for-
f free acid.

nder ordinary conditions, this reaction occurs so slowly that it
e detected.   If, however, the action of the hydrogen is acceler-
the presence of a catalyser, *e.g.* metallic platinum, the action
etected.

ie dissolution of metals in nitric acid is accompanied
n of a portion of the acid.   The process can be ref

the scheme given on p. 607, if we write nitric acid as a hydroxyl compound of pentavalent nitrogen   The series is —

Nitric acid, $HNO_3 + 2H_2O$ $- N \cdot OH_5$
Nitrogen peroxide, $NO_2 + 2H_2O - N \cdot OH_4$
Nitrous acid, $HNO_2 + H_2O$ $- N \cdot OH_3$
Nitric oxide, $NO + H_2O$ $N \cdot OH_2$
Hyponitrous acid, $\frac{1}{2}H_2N_2O_2$ $- N \cdot OH$
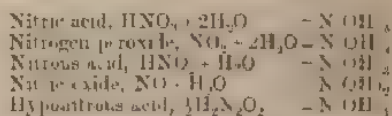
In the oxidising action of nitric acid, from one to four oxidation units can take part, depending on which of the lower members the acid is converted into, and the equation has to be written accordingly   If for example, it is desired to express the oxidation of copper to cuprion with formation of nitric oxide (which is the predominant reaction on treating copper with nitric acid), we have the following   Each mole of copper requires two units in order to pass into dicuprion ; one mole of nitric acid, however, yields three units.   Consequently we must allow two moles of nitric acid to react with three of copper The three moles of copper, however, require further six moles of nitric acid in order to pass into normal nitrate ; altogether then, eight moles of nitric acid act on three of copper .

$$3Cu + 8HNO_3 - 3Cu(NO_3)_2 + 2NO   4H_2O.$$
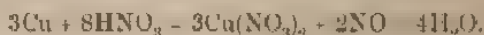
* Similarly, it is found that sulphuric acid on passing into sulphurous acid, yields two oxidation units, and these are exactly sufficient to convert one mole of copper into dicuprion.   One mole more of sulphuric acid serves for the formation of the salt, so that we finally have

$$Cu + 2H_2SO_4   CuSO_4 + SO_2 + 2H_2O.$$
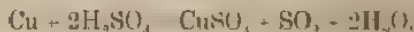
In its solutions, dicuprion is greenish blue in colour.   If any other colour is shown by a cupric salt, we must conclude that the undissociated portion of the salt is also coloured.   This is, as a matter of fact, often the case.

For the higher organisms, dicuprion is a rather powerful poison while moulds, for example, can flourish in presence of copper salts

The heat of formation of dicuprion from the metal amounts to 66 kj , it is therefore negative, while that of the metallic cations hitherto considered was positive.   The difficulty of the formation of the ion from the metal, and the ease of the reverse transformation which we meet with in the case of copper, are connected with this fact

630. **Copper Hydroxide.**—From the solutions of cupric salts strong bases precipitate *cupric hydroxide*, $Cu(OH)_2$ as a bright blue substance, which on being kept for some time under the solution, more quickly on heating, becomes dark brown, at the same time losing water and passing into *cupric oxide*, CuO.   It may be asked how it is possible for a substance to lose water while lying under water, of which it has

therefore as much at its disposal as it requires. The answer is that cupric hydroxide is not at all a stable compound at the ordinary and higher temperatures, and the fact that it is produced before the form which is most stable under the conditions, viz. copper oxide and water, is a case of the law of the prior formation of the unstable forms.

Copper hydroxide is not soluble in alkalis except in very small amount, when the solvent is very concentrated. In the presence of many organic substances it dissolves with formation of complex compounds of dark blue colour. Ammonia also precipitates cupric salts with formation of hydroxide; an excess, however, again effects dissolution. The liquid thereby becomes of a dark corn flower blue. This is a sign that a new ion has been produced; as a matter of fact, from the dark blue solutions salts can be obtained in the solid state containing the cation $Cu(NH_3)_4$.

Copper hydroxide is not a strong base; it is one of the weakest of the hydroxides of the divalent ions. This is shown in the distinct hydrolysis of its salts, in consequence of which the solutions of the salts of strong acids all react acid. Cupric salts of weak acids exhibit phenomena of decomposition; some, e.g. the carbonate, cannot be obtained at all in the normal condition, but only salts containing hydroxyl, or basic salts, are known.

Besides being formed by the decomposition of cupric salts, copper oxide is also obtained by the direct oxidation of copper in the air at a low red heat. Cuprous oxide, the anhydride of cuprous hydroxide (v. infra), is first formed, but this also passes into cupric oxide under the above conditions.

Copper oxide is very readily reduced to the metal by means of hydrogen with production of water. It has already been mentioned that this reaction was used in order to determine the ratio of combination between hydrogen and oxygen. This same property of ready reducibility conditions the use of copper oxide in *organic elementary analysis*. The substance to be investigated is mixed with excess of copper oxide, the mixture placed in a tube and the whole heated, after absorption apparatus for water (calcium chloride) and for carbon dioxide (caustic potash or soda lime) have been attached. By means of the oxygen of the copper oxide the carbon of the organic compound is burned to carbon dioxide, the hydrogen to water. These products are collected and weighed, and from this the amount of the above elements contained in the organic compound (also weighed) can be determined.

Any nitrogen which is present is evolved in the free state, and the amount can also be determined by collecting and measuring the gas.

641. Cupric Chloride.—Anhydrous *cupric chloride*, $CuCl_2$, is formed by the combustion of copper in a current of chlorine, as a yellow brown powder which dissolves in anhydrous solvents with a dark yellow colour, whereas its aqueous solution is blue or green.

according to the concentration. From the solution the salt with $2H_2O$ crystallises out; on account of adhering mother liquor, it generally appears green, but in the pure state it is bright blue. The hydrated salt on being heated loses hydrogen chloride along with the water, like many of the other chlorides of this group, and is converted into an oxychloride. The anhydrous salt experiences the same transformation on being heated in oxygen; chlorine is evolved at the same time: $4CuCl_2 + O_2 = 2Cu_2OCl_2 + 2Cl_2$. By means of hydrogen chloride the oxychloride is again converted into the chloride: $Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O$. This reaction is made use of for the manufacture of chlorine; the catalytic acceleration of the oxidation of hydrogen chloride with free oxygen (p. 169), also, is attributed to the alternate occurrence of these two processes in the mixture of oxygen and hydrogen chloride, but this view still lacks experimental foundation.

Concentrated aqueous solutions of copper chloride appear green. If fuming hydrochloric acid is added, a yellow-brown liquid is obtained. The latter colour is the individual colour of the undissociated copper chloride, the dissociation of which is reduced almost to zero by the large excess of chloridion. So long as considerable amounts of undissociated salt are present in the fairly concentrated solutions, the mixed colour formed by the yellow of the chloride and the blue of the dicuprion is produced. Very dilute solutions in which the dicuprion predominates, exhibit the blue colour of that ion. On being heated, dissociation is diminished; the yellow colour of the undissociated salt appears also to become more intense (p. 631), so that for this reason also, the solutions change colour towards the green. If we write with a solution of copper chloride on paper, the characters become yellow on being heated at those parts where the strongly coloured, anhydrous salt is formed, and on cooling disappear again where the pale-blue coloured hydrated salt is formed through the attraction of moisture from the air. This solution can therefore also be used as a "sympathetic ink" (p. 621), but must not be applied with a steel pen because iron acts on solutions of copper with precipitation of this metal.

As has just been mentioned, cupric chloride readily forms oxychlorides with loss of chlorine. These compounds vary in composition according to the conditions of formation. The one best characterised is the compound $Cu_2Cl(OH)_3$, which occurs in nature as *atacamite*, and is also readily formed where chlorine compounds, water and oxygen act on copper. It is a bright green substance which forms rhombic crystals, and is scarcely soluble in water. It dissolves readily in acids and in ammonia, as indeed could be expected from its composition.

632. **Copper Sulphate.**—Cupric sulphate or *copper vitriol*, $CuSO_4$, is obtained on the large scale by the oxidation of naturally occurring sulphur compounds of copper. It is a salt which crystallises in blue triclinic crystals with $5H_2O$, and which is similar to the other

vitriols" in its properties. According to the temperature, the salt takes up other quantities of water and exhibits forms which occur in the case of the sulphates of other divalent metals (cf. p. 578). It also crystallises along with potassium and ammonium sulphate in double salts with $6H_2O$. The water of crystallisation passes off fairly readily, that with $1H_2O$ at first remaining behind, which is more difficult to dehydrate. The anhydrous sulphate is dirty white in colour; in the air it absorbs water and again becomes blue. The dehydrated copper sulphate is sometimes used as a desiccating agent, especially for liquids, on account of the convenience of being able to tell when the desiccation is complete, from the non-appearance of the blue colour in freshly dried sulphate.

If an *electric current* is passed through a solution of copper sulphate, metallic copper is deposited as a coherent coating on the cathode. As it is particularly easy to obtain a good precipitate with copper (p. ...), the process is made use of not only for coating other objects with copper, but also for shaping objects in copper, and thus of producing a sort of cold metallic casting. The deposit fills out very exactly the form of the cathode, and when it has acquired a certain thickness it can be removed as a coherent mass. For this reason it is used for taking casts of printing blocks. These are first cut in wood and then cast in warm gutta-percha or in very readily fusible metal (cf. bismuth), and the cast is then made the cathode of an electric current in a solution of copper sulphate. The anode consists of copper in order that the amount of copper contained in the solution shall remain unchanged (p. 625). Non-conducting casts, such as those of gutta-percha or gypsum, are first covered with a conducting layer, *e.g.* by rubbing with graphite.

The same process is made use of for the purpose of *purifying* impure copper. The impure copper is then made the anode, and a thin sheet of pure copper is used for the cathode. On this, very pure copper, "electrolytic copper," is deposited if a current of very small potential is employed, for the impurities either are not dissolved, but sink to the bottom as "anode mud," or they are not separated out at the cathode (e.g. iron), and must be removed from the solution when they have accumulated too much. The copper, for example, which is used for electrical purposes, and which must be very pure, is treated in this way.

One can spare one's self the special generation of an electric current by making the separation of copper a part of the reactions in a voltaic cell. As a matter of fact, the process of electrical copper casting, called *electrotyping*, was discovered through copper sulphate being used as an oxidising agent in a voltaic cell, whereby the deposited copper took the exact shape of the cathode.

Such a cell is represented in Fig. 118. K is the cathode of copper, z a porous cell of fired clay which allows the current to pass, but

checks the mixing of the liquids, and Z is an anode of metallic z
K is surrounded by a solution of copper sulphate, Z by a soluti...
zinc sulphate   When, then, K and Z are connected by a metallic co
ductor L, the deposition of copper on K occurs, while an equiva...
amount of zinc is at the same time dissolved from Z.   During th
process an electric current passes through the conductor in the dire

tion of the arrow, and can be eas...
detected and measured by inserting
current indicator in the circuit.
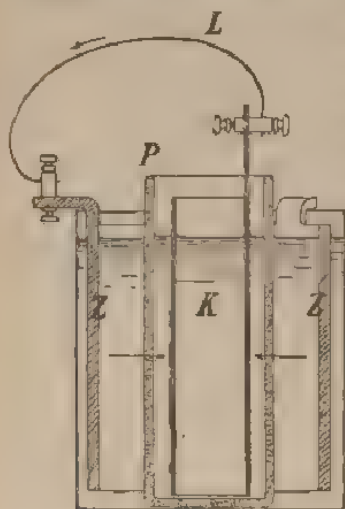
The chemical process, therefo...
consists in metallic copper being de...
posited from the copper sulphate an...
zinc dissolving to zinc sulphate. I...
we write the equation of the ions w...
have first of all $Cu + SO_4 + Zn =$
$Cu + Zn + SO_4$, omitting on eith...
side the ion SO_4'', which remain...
unchanged, we obtain $Cu + Zn =$
$Cu + Zn$.   The process, therefor...
simply consists in the copper an...
zinc exchanging their rôle as ions, a...
since the ionic state is determined b...
the positive electrical charge, in th...
cuprion yielding up its charge to th...
zinc, which thereby passes into zinc io...
while the copper is deposited in th...
metallic state

Fig. 118.

This process immediately occurs when metallic zinc is introduce
into a solution of copper sulphate; copper is deposited and zinc...
dissolved.   An electrical current cannot, however, be obtained in th...
way.   The reason of this is that the transference of the charges take...
place everywhere *within* the liquid, so that it is not possible to la...
hold of and conduct the electrical movement.   In the arrangemen...
shown in Fig. 118, which is called after its discoverer, the *Daniell* ce...
the solution of the zinc and the deposition of the copper take place a...
separate points, and this becomes possible only when the necessar...
equalisation of electricity occurs through the medium of the liquid o...
the one hand, and of the conductor on the other

633. **Voltaic Cells.**— In order that the above process, whereby a
electric current is generated in the Daniell cell, may occur, it is evide...
that the reactions on which the cell is based should occur even wit...
out this special arrangement, since there would otherwise be no cau...
to make the process take place   Now, however, only those process...
occur in which free energy is available ; a voltaic cell is therefore a...
apparatus by means of which free chemical energy is converted int...
free electrical energy.

It will therefore be possible to construct other cells after the pattern of the Daniell, by replacing the zinc and the copper by other metals placed in solutions of their salts and connected with one another. This is, as a matter of fact, the case; with every such combination a cell is obtained in which one of the metals is reduced from its salt and deposited in the metallic state, while the other is consumed, i.e. is dissolved as ion. Which of the two connected metals will assume one or the other rôle, is found by introducing each metal into the solution of the other; one of the metals will then precipitate the other from its solution, while the other metal will leave the solution of the first unchanged. The precipitating metal is then always the anode, which also dissolves in the cell the same as in the direct experiment, and the precipitated metal is the cathode, for it is deposited in the cell in the same way as in the direct action. From these experiments it is found that a given metal can both precipitate and be precipitated; cadmium eliminates copper from solutions of copper salts, but is deposited from its solutions in the metallic state by zinc.

The law which obtains here can be expressed as follows. *It is possible to arrange all the metals in a single series in such a way that each precipitates all the metals following from their aqueous solutions, but is precipitated by each of the preceding ones.* On account of the electrical relations of this series, to be presently mentioned, it is called the *tension series* of the metals.

634. Electrical Potential. — The work which an electric current can perform depends not only on the strength of the current or the amount of electricity which in unit of time passes through a section of the conductor, but on another magnitude as well, which is called the *potential*, the unit of which, fixed once for all, is called the *volt*. Thus an electric incandescent lamp, which is supplied by a current of one ampere (p. 196) at a potential of 50 volts, gives the same light as a lamp which uses a current of 5 amperes at 10 volts, while at a potential of 200 volts a current of 0·25 ampere is sufficient to produce the same effect.

From this example it is at once seen that the electrical work of a current is measured by the *product of strength of current and potential.* This has a great similarity to the performance of work by a falling mass of water; in this case also the work depends on the quantity of the water and on the height of fall, and the amount of work which can be obtained with the same quantity of water is all the greater the greater the height through which the water falls. To the *quantity of water* there corresponds the magnitude, which has been called *quantity of electricity*, and which can be measured, in accordance with Faraday's law (p. 197), by the amount of substance separated electrolytically on inserting an electrolytic cell in the circuit. To the *height of fall* there corresponds the property of electrical energy, which has just been

is filled with pure water, it behaves essentially like any ordinary clay cell, for under slight pressure the water flows through, only more slowly than when the precipitate is absent. If, however, instead of the pure water an aqueous solution, e.g. of ordinary sugar, is placed in the cell, this does not, in the first instance, filter through. If the pressure is increased, percolation commences at a definite pressure, but it is not the sugar solution that filters through, but pure water.

If the experiment is performed with different solutions of sugar, it is found that a definite pressure is necessary in each case in order that the water may pass through, and this pressure is proportional to the concentration of the solution.

If, after being closed and a manometer attached, the cell is placed in pure water, the latter continues to pass through the cell wall until the same pressure is produced as that under which the water could be forced through the cell-wall.

Various other substances behave in a manner similar to sugar; they are kept back by the cell wall and generate a pressure. There are substances, however, which are not kept back by the cell wall; these, also, do not generate a pressure (or only a comparatively small one, when they are partially retained).

We must conclude, therefore, that the pressure is due to the dissolved substance; the water cannot give rise to it because it can pass through the cell-wall.

On comparing solutions of different substances which do not pass through the cell wall, with respect to the pressure which they produce, it is found that *the same pressure is produced by those solutions the concentrations of which are in the ratio of the molar weights of the dissolved substances.* These pressures, therefore, which are called *osmotic pressures*, could be used for the determination of the molar weight of dissolved substances, in the same manner as the depression of the freezing point and the lowering of the vapour pressure (p. 153). The experimental difficulties in the carrying out of such measurements, however, are very great.

The temperature exercises an influence on the osmotic pressure; under ordinary conditions, the latter increases about ⅓rd per cent for every degree.

On the whole, therefore, the osmotic pressure follows similar laws to the gas pressure; the latter is also proportional to the concentration or density of the gas (Boyle's law, p. 68), and for every degree increases by 1/273, i.e. about ⅓rd per cent (Gay Lussac's law, p. 49).

The resemblance, however, extends still further. If, for example, the osmotic pressure is determined which is exerted by a definite solution of carbon dioxide, it is found to be just as great as that exerted by the same amount of carbon dioxide when it occupies in the gaseous state the same volume as the solution. Thus far, therefore, a dissolved substance behaves as a gas, and its osmotic

electrical potential is at the present time the most fruitful method of determining this important and not easily accessible magnitude.

On constructing cells containing the above three metals and also the other possible cells, the following values of the potentials are obtained —

Silver-copper	. . .	0·17 volt
Silver-cadmium .	. . .	1·22 ,,
Copper-cadmium	. . .	0·75 ,,

On comparing these values with the former, it is found that the potential of the combination silver-zinc is equal to the sum of the potentials silver-copper plus copper-zinc or silver-cadmium plus cadmium-zinc, etc. Writing the values

Silver	= 1·57 volt
Copper	= 1·10 ,,
Cadmium	= 0·35 ,,
Zinc	= 0·00 ,,

we find that the potential of any combination of these metals is equal to the difference of the corresponding numbers. These numbers may therefore be called the *potentials of the single metals*, in which case, naturally, the zero, Zn - 0, has been arbitrarily chosen. This, however, has no influence on the result, for if any other metal is put equal to zero, and the corresponding values of the potential are calculated with due regard to the sign, another series is obtained which exhibits the same differences between the separate members, and has the same meaning, therefore, as the former series.

This series is the numerical expression of the potential series (p. 464), it is the expression of a fundamental property of the metals.

The numbers depend on the temperatures, but their relative positions do not greatly change within the range of temperatures investigated; as regards this point, however, our knowledge is as yet rather scanty.

The following table gives a more complete list of potentials. In this case zinc has not been taken as the zero, but another zero has been chosen, which gives expression to the actual change of the free energy in the passage from the metallic to the ionic state. We cannot explain here how this zero has been derived, and this is of no importance, in the first instance, since we are concerned only with the differences, and these are independent of the zero.

Cæsium			Tin	
Rubidium			Lead	0·10 volt
Potassium			Hydrogen	0·25 ,,
Sodium			Antimony	
Magnesium	1·24 volt		Bismuth	
Aluminium	1·03 ,,		Arsenic	
Manganese	0·82 ,,		Copper	− 0·59 ,,
Zinc	0·51 ,,		Mercury	− 1·03 ,,
Cadmium	0·36 ,,		Silver	1·06 ,,
Thallium	0·11 ,,		Palladium	1·07 ,,
Iron	0·12 ,,		Platinum	
Cobalt	0·02 ,,		Gold	
Nickel	0·02 ,,			

cuprous oxide. On being further heated in the air, it is converted into black cupric oxide; on removing this black coating, however, the piece of oxidised copper, it is found to be generally red on the side next the metal, *i.e.* to consist of cuprous oxide.

The corresponding *cuprous hydroxide*, $Cu_2(OH)_2$, or $CuOH$, obtained as a brick red powder by the decomposition of the chloride, to be presently mentioned, with caustic potash or soda.

In nature cuprous oxide occurs as *red copper ore*, and is a highly valued ore on account of its richness in copper; it can be converted into metallic copper by reduction with charcoal.

Cuprous oxide is also formed as the product of reduction of Fehling's solution with grape-sugar and similar substances (p.), and can be prepared in this way. In moist air it is oxidised to cupric or to basic carbonate.

On treating cupric oxide or hydroxide with acids, not the corresponding cuprous, but the cupric salts, are generally formed, and part of the copper is deposited in the metallic state as a blackish powder. With sulphuric acid, for example, the reaction takes place according to the equation $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. On considering the ions the process can be interpreted as taking place in such that cuprous sulphate is first formed, the monocuprion of which however immediately undergoes transformation into dicuprion and metallic copper: $2Cu = Cu + Cu$. The solution contains so to a preponderating extent, but it is in accordance with the relations to assume that it is a case of chemical equilibrium between the two ions and the metallic copper, in which a large concentration of dicuprion is opposed by a very slight concentration of monocuprion.

If instead of sulphuric acid a halogen hydracid, thiocyanic acid, some other acid which can form a very difficultly soluble cuprous salt is taken, the above decomposition does not take place, and the active cuprous compounds are formed. This is explained by the fact that monocuprion is present only in a negligibly small amount in the solution produced, since, of course, the salts are difficultly soluble; decomposition of monocuprion into dicuprion and metal can therefore take place only to an inappreciably slight extent.

612 Cuprous Chloride is a white salt, only very slightly soluble in water; it can be obtained by boiling a solution of cupric chloride in strong hydrochloric acid with copper powder. The colour at first darkens, but a yellowish liquid is finally obtained, which on being poured into much water deposits a snow white precipitate of cuprous chloride. This must be washed as far as possible with exclusion of air, as it otherwise rapidly passes into cupric oxychloride (p. 640).

This reaction is the reverse of the one given before; whereas in the previous case monocuprion decomposes into dicuprion and metallic copper, we have in this case the reverse transformation of cupric salt with metallic copper into cuprous salt. The reason is that in

drochloric acid solution monocuprion is present only in very slight amount, and further, the fact that cuprous chloride, which is almost insoluble in water, dissolves in hydrochloric acid, proves that in this case the chloride is either dissolved as such (without dissociation), or that a compound of the two constituents, a hydrochlorocupric acid, has been formed No investigation has as yet been carried out as to how far the one or the other possibility predominates.

In ammonia also cuprous chloride dissolves to a colourless liquid, in which cuproammonion, $Cu(NH_3)$, is contained The chloride of this ion, $CuNH_3Cl$, can be obtained in colourless, regular crystals by boiling a solution of ammonium chloride with copper powder and allowing the liquid produced to cool slowly. The aqueous solution becomes almost immediately blue in the air, oxygen being absorbed.

Both solutions of cuprous chloride, the acid as well as the ammoniacal, absorb a considerable amount of *carbon monoxide*. This appears to be rather firmly bound, but can be removed from the liquid by continued pumping. We are dealing in this case with the formation of a complex cation, similar to the complex ion produced from diferrion and nitric oxide (p 591), which, like this, is not very stable, and possesses an appreciable dissociation pressure. The reaction is used for the determination of carbon monoxide in gaseous mixtures, but must, for the reasons just mentioned, be employed with some care.

643. Cuprous Bromide, $CuBr$, is very similar to cuprous iodide

644 Cuprous Iodide is formed along with free iodine, when dicuprion and iodidion come together in solution, according to the equation $2Cu^{..} + 4I = 2CuI + I_2$. In this process we can regard the dicuprion as losing a positive charge, and thereby neutralising the negative charge of one iodidion The monocuprion produced at once forms solid cuprous iodide, with a second quantity of iodidion, and separates out If a reducing agent is added at the commencement, whereby the dicuprion can be converted to monocuprion, cuprous iodide alone without free iodine is deposited. This is effected, for example, by sulphurous acid or an acid solution of ferrous sulphate.

Since the cuprous iodide is soluble only to an exceedingly slight extent even very small quantities of iodine can in this way be separated from a solution, and the method is employed commercially for obtaining iodine from the mother liquors containing iodidion along with comparatively large quantities of other halogens

Cuprous iodide is a reddish white, heavy powder which yields cupric oxide and iodine by distillation with pyrolusite, and potassium iodide and cuprous oxide by boiling with caustic potash It dissolves in ammonia similarly to cuprous chloride

* The interaction between iodidion and dicuprion, described above, does not occur instantaneously, but with a measurable velocity which becomes very small with increasing dilution Thus very dilute solutions

...

Copper Thiocyanate. ...

Other Cuprous Compounds — ...

517 Complex Copper Compounds. We have already ... of the formation of a complex compound of chromium, and ... which is characterised by the production of a dark blue colour ... the mixed solution. In this the new ion $CuNH_4$ ... is present ... salts of which are obtained by adding excess of ammonia to solutions of the respective copper salts.

Of these salts the best known is the sulphate, $CuNH_4...S...$ which is easily obtained by adding ammonia to a concentrated solution of copper sulphate until the solution has again become quite clear, then pouring a layer of alcohol on the top. The salt is only slightly soluble in alcohol, and is deposited in well formed, dark ... crystals as the alcohol slowly diffuses into the underlying ... the same way various other salts of the same ion can be obtained. Solutions of these salts are used in combating certain parasites found on vines.

Copper forms other complex compounds of a similar co...

adding excess of alkali to cupric salts in presence of certain organic compounds, e.g. sugar or tartaric acid. In this case also a dark blue liquid is produced from which a salt of the same colour can be obtained. In these salts acids containing copper are present, the composition of which depends on that of the substance employed, and cannot be discussed here. In general the property of forming such compounds is found in the same organic hydroxyl compounds as hinder the precipitation of ferric oxide by bases (p. 592).

Of such compounds the best known is *Fehling's solution*, which is obtained by adding *tartaric acid* and excess of caustic potash to a solution of copper sulphate. It is a dark blue liquid, which is changed by various reducing agents in such a manner that it deposits a precipitate of red cuprous oxide (p. 650). It can serve, therefore, for the detection of such substances, and it is used for this purpose in analysis, e.g. for the detection of grape-sugar in urine.

In the cuprous series some complex copper compounds have been already mentioned. It has still to be remarked that cuprous cyanide dissolves in potassium cyanide to form a colourless liquid, from which the complex salt $KCu(CN)_2$, the potassium salt of cuprocyanidion, is obtained. This solution is very stable, and contains exceedingly little cuprion, so that all solid copper compounds, even copper sulphide, dissolve in potassium cyanide with formation of this complex salt. Advantage is also taken of this behaviour in analysis.

Copper also forms a number of complex compounds in which sulphur plays a part, and which are derived from sulphurous and thiosulphuric acids. This reference to their existence must suffice here.

648. **Metallurgy of Copper**. —On account of the large consumption of copper in the arts, its manufacture from the naturally occurring ores is an important industry. So long as we are dealing with oxygen ores, red copper ore, or the basic carbonates, reduction with charcoal, which takes place very readily, is all that is necessary. In the case of the sulphurous ores, the most important of which are *copper pyrites* and *variegated copper ore*, the task is more complicated. For these ores are compounds of copper sulphide with iron sulphide, so the preparation of pure copper requires at the same time the elimination of sulphur and iron. This is rendered more difficult by the fact that the sulphur combines much more firmly with copper than with iron, so that it can be removed only with difficulty. On being subjected to an oxidising process of roasting, ferrosoferric oxide is chiefly formed along with cuprous sulphide, and by fusing this mixture with the addition of siliceous substances, a slag consisting essentially of iron silicate and a mixture or an alloy of copper and cuprous sulphide is obtained by repeating the operation. When the amount of sulphur has become sufficiently small, the crude copper (black copper) is cast into plates and subjected to electrolysis in an acid solution of copper sulphate, with a piece of copper foil as cathode.

In this way pure copper is obtained, and the copper sulphide, which along with the other impurities forms the anode mud, is again fused along with other portions of the ore.

The development of the method of electrolytic deposition has further led to the extraction of the copper ores in the wet way, the metal being separated electrolytically from the solutions of copper salt obtained. For this purpose ferric salts are mostly used, which dissolve the cuprous sulphide with formation of cuprous salt, themselves being reduced to ferrous salts, and sulphur being deposited.

On re-fusing the copper cuprous oxide is formed, which dissolves in the liquid metal, but on cooling again separates out and renders it brittle. For this reason the copper directly before being cast must be subjected to a reducing treatment (stirring with a pole of wet wood). If the reduction is carried too far the tenacity of the copper is impaired, presumably through the conversion of traces of other metallic oxides into the metallic state. This last operation must, therefore be performed with care and frequent sampling.

CHAPTER XXXIII

LEAD

649. General.— Lead is allied to strontium and barium in like manner as zinc and cadmium are allied to magnesium. Calcium, which exhibits relations of isomorphism in both directions, stands in the middle. On the other hand, lead is decidedly a heavy metal, and forms an insoluble, dark coloured sulphur compound.

In nature lead is fairly widely distributed. Its most important naturally occurring ore is *lead sulphide*, from which by far the largest amount of the metal is obtained. The carbonate and the sulphate, which are isomorphous with the corresponding salts of strontium and barium, are also found.

Metallic lead has been known from olden times, as it can be readily obtained from its ores. Its many applications depend, on the one hand, on its low melting point, 330°, and its great density, 11·4, and, on the other hand, on its softness and consequent plasticity. The last property renders it possible, especially at a somewhat higher temperature, to form lead by pressure like a plastic mass, and in this way to produce wire, tubing, and such like.

In moist air lead oxidises very rapidly, but only superficially, so that on the whole it is fairly resistant. It should be mentioned here that it resists the action of perfectly pure water much less than that of ordinary spring or river water. This is due to the fact that in the former case, under the joint action of water and atmospheric oxygen, lead hydroxide is produced, which is slightly soluble in water, and therefore does not protect the lead. In impure water, which contains sulphanion and carbanion, the corresponding lead salts are formed, which have an extremely small solubility, and form a firmly adhering layer on the lead. Thus lead pipes can be quite well used for the ordinary water-supply, but not for distilled water.

The combining weight of lead has been determined by the conversion of the metal into the oxide, and *vice versa*. It has been found to be Pb = 206·9.

650. Plumbion.—Lead forms only one divalent elementary ion, but besides this several containing oxygen, and also complex ions.

Plumbion, $Pb^{..}$, is colourless, and in its compounds resembles barium in many respects. It is a powerful poison for higher organisms, and through accumulation is very harmful when repeatedly taken into the system even in small doses. For this reason workmen who have to work with lead are constantly exposed to the poisonous action, and great attention and cleanliness are required in order to resist the danger.

The heat of formation of plumbion from the metal is + 2 k.

Corresponding to its position in the potential series, lead has no special tendency to pass into the ionic state. Free acids are not appreciably decomposed by lead, so that oxidising agents must be employed in order to dissolve it. The best solvent for metallic lead is nitric acid, which forms one of the few readily soluble lead salts, most of the lead salts being difficultly soluble.

From the solutions of the salts, bases give a white, flocculent precipitate of *lead hydroxide*, $Pb(OH)_2$, which does not dissolve in excess of ammonia, but is soluble in excess of alkali. The reason is the same as in the case of alumina, which behaves in a similar manner. By splitting off hydrion, lead hydroxide can form anions of the composition PbO_2'' and $HPbO_2'$, the alkali salts of which are soluble in water.

Lead hydroxide is slightly soluble in water. It is readily formed when lead, water, and atmospheric oxygen come together. Strange to say, in this oxidation, as in many others which occur with free oxygen in presence of water, hydrogen peroxide is formed at the same time. Measurements have shown that the amount of peroxide corresponds to that of the lead hydroxide, so that the reaction has to be written as follows:

$$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2.$$
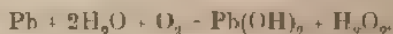
* It is probable that the first product of the reaction is a single substance, perhaps a compound $Pb(OH)_4$, which decomposes into $Pb(OH)_2$ and H_2O_2. This reaction would then be another example of the fact that the unstable compounds are usually formed before the stable. This view, however, is rendered somewhat doubtful by the properties of the anhydride of the assumed compound $Pb(OH)_4$, or lead peroxide PbO_2, which is a well known stable substance.

* The formation of hydrogen peroxide, or of other compounds belonging to the peroxide type, has been proved in the case of most oxidations by free oxygen, so that it appears to be the rule. The peroxide, certainly, generally decomposes so rapidly with evolution of free oxygen that its whole amount can never be determined, and only very slight traces are found if special precautions are not observed. The rational interpretation of these long neglected but very general phenomena is given by the law above mentioned of the occurrence of the unstable forms together with "coupling" (p. 206).

Lead hydroxide loses water very readily and passes into the part

low coloured lead oxide, PbO. The same compound is obtained in any desired amount by heating lead to above its melting point in the air; if the temperature is raised above its melting point, it forms a pale yellow, lustrous scales, and in ordinary life is called *litharge*. It is used for many purposes in the arts, *e.g.* in the manufacture of glass, for the preparation of varnish, in dyeing, etc.

651. **Lead Chloride**, $PbCl_2$, is slightly soluble in cold water, more soluble in hot, and crystallises in anhydrous needles. It unites with lead oxide to form basic salts, which are obtained by heating ammonium chloride with litharge; they are of a pale yellow colour, and are used as a pigment under the name *Naples yellow*.

Lead bromide is similar to the chloride, only still less soluble.

Lead iodide, PbI_2, is still more difficultly soluble. It crystallises from hot saturated solutions in laminae of a gold lustre; precipitated from a dissolved lead salt in the cold by means of an iodide, it is formed as a yellow powder. It undergoes slight decomposition in light, so that a mixture of lead iodide and starch when exposed to sunlight rapidly becomes dark through formation of starch iodide. It unites with potassium iodide to form a double salt, which is stable only in contact with solutions which contain a large excess of potassium iodide; it is decomposed by pure water with separation of lead iodide.

652. **Lead Nitrate**, $Pb(NO_3)_2$, crystallises anhydrous in forms of the regular system, and is isomorphous with barium nitrate. It is easily obtained by dissolving lead or lead oxide in dilute nitric acid; by concentrated acid it is precipitated from its solutions, owing to the increase of the concentration of nitranion. Strong nitric acid is therefore almost without action on the metal, because the nitrate produced forms a protecting layer.

On being heated, lead nitrate decomposes into lead oxide, oxygen, and nitrogen peroxide: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$. This behaviour is made use of for the preparation of nitrogen peroxide (p. 329).

653. **Lead Sulphate**, $PbSO_4$, is a white salt extremely difficultly soluble in water, and is always formed when plumbion and sulphanion come together in solution. It is very similar to barium sulphate, but by reason of its greater density it is deposited more rapidly than it from solutions. It is readily soluble in a solution of ammonium tartrate containing excess of ammonia, and is thereby easily distinguished from barium sulphate. This solubility depends on the formation of a complex salt, the lead uniting with the anion of tartaric acid to form a complex compound. This, again, is another case of the formation of organic hydroxyl compounds containing metals, which has been several times mentioned (pp. 581 and 653). Since plumbion is withdrawn from the solution through the formation of this complex, lead sulphate must pass into solution in order to cover the loss, and this goes on either until all the lead sulphate is dissolved, or until

2 U

chemical equilibrium has been established between the differ[...]
ponents of the solution and the solid salt.

Lead sulphate occurs in nature in rhombic crystals which [...]
morphous with those of heavy spar and celestine, and which [...]
anglesite or *lead vitriol*. The salt also occurs as an intermedia[...]
duct in working up lead sulphide for metallic lead.

To the difficult solubility of lead sulphate is due the use [...]
for lining the reaction chambers and concentrating pans used [...]
manufacture of sulphuric acid (p. 289).   Under the action [...]
the metal very rapidly becomes covered with a firm layer of [...]
which protects the underlying metal.

Lead sulphate is appreciably soluble in concentrated [...]
acid, and crude sulphuric acid almost always contains a large [...]
of lead.   Whether this is due to the formation of acid [...]
$PbH_2(SO_4)_2$, or whether sulphuric acid is a solvent for lead [...]
such, has not yet been decided.   On diluting with water the [...]
sulphate is again precipitated, since, owing to the presence [...]
phanion, it is still less soluble in dilute sulphuric acid than [...]
water

* This behaviour, viz. that the solubility of a salt in water [...]
diminished and then increased by the addition of its acid, [...]
general.   The diminution is a regular phenomenon; it is due [...]
just been said, to the presence of the anion by reason of which [...]
solubility product is reached even at a much smaller concentra[...]
the cation (by which the solubility of the salt is here measured[...]
frequently occurring increase of the solubility in very conc[...]
acid has generally its cause in the formation of a new soluble [...]
pound between acid and salt.

On account of its difficult solubility, lead sulphate is used for [...]
separation of plumbion from its solutions in qualitative and qua[...]
tive analysis.   In order that nothing may be lost in the wash[...]
sulphate is first washed with dilute sulphuric acid, and this [...]
displaced by alcohol, in which the sulphate is much less soluble [...]
water.

654. Lead Chromate.—On mixing solutions containing [...]
manion and plumbion, a yellow precipitate of *lead chromate* is [...]
which is very difficultly soluble in water, and which, on account [...]
strong colour, is used as a pigment under the name *chrome* [...]
When mixed with Prussian blue, chrome yellow gives a hue [...]
colour called "*green cinnabar.*"   Basic lead chromate has a [...]
red to carmine-red colour, and is also used as a pigment [...]
name *chrome orange* and *chrome red*.

The same precipitate of normal lead chromate is also obtained [...]
using a solution of a *dichromate* as the precipitant; hydrion is [...]
produced, and the solution reacts acid   The details of this pro[...]
exactly the same as in the case of the precipitation of *barium* [...]

ith dichromates (p. 617). If the anion of the lead salt is that of a strong acid, the precipitation under these conditions remains incomplete, since the hydrion formed reduces the concentration of the chromanion and increases that of dichromanion to such an extent that the solubility product of lead chromate is no longer reached. If, however, the lead salt of a weak acid is employed, e.g. lead acetate, precipitation is practically complete, because the hydrion produced is for the most part converted into undissociated acetic acid.

Lead chromate dissolves in strong bases with formation of a yellow salt. Since chromanion is contained in this, the plumbion must have also disappeared, as otherwise solution would be impossible. As a matter of fact, the cation, $Pb^{..}$, is converted into the anion PbO_2'' (p. 656) under the influence of the large amount of hydroxidion present: $Pb^{..} + 4OH' = PbO_2'' + 2H_2O$.

This behaviour is evidently a general one; all hydroxides which, like lead hydroxide, possess both basic and acid properties, must exhibit the same reaction, i.e. the difficultly soluble salts which they form with any acids are dissolved by alkalis. This is, as a matter of fact, the case; thus, the difficultly soluble salts of alumina, such as the phosphate, dissolve readily in a solution of caustic potash.

Besides being used as a dye, lead chromate is also employed in the laboratory, similarly to copper oxide, as an oxidising agent in the elementary analysis of organic substances.

655. **Lead Acetate**, $Pb(C_2O_2H_3)_2$ $3H_2O$, or sugar of lead (so called from its sweet taste), is, of all the lead salts, the one most used in the arts, since it is readily soluble, and therefore allows of the employment of plumbion where necessary. It is obtained by the action of crude acetic acid on lead oxide, the salt being purified by crystallisation.

Lead acetate is very readily soluble in water; its solutions are generally slightly turbid owing to the presence of a white precipitate. The latter consists of lead carbonate, which is formed by the action of the carbonic acid in the air on the salt; this action is facilitated by the volatility of acetic acid.

If carbon dioxide is passed into a solution of lead acetate, lead carbonate is immediately deposited as a white, crystalline precipitate. The reaction is, however, not complete, and an equilibrium is finally produced in the solution between the remaining plumbion, acetanion, carbanion, hydrion, and the undissociated substances produced from these ions. No carbonate is precipitated by carbon dioxide from the lead salts of strong acids, e.g. lead nitrate, nor from the acetate if sufficient acetic acid has been added at the commencement.

The relations obtaining here are fairly similar to those found in the precipitation of the zinc salts by sulphuretted hydrogen (p. 633), only that in this case a much smaller concentration of hydrion is sufficient for equilibrium.

Lead oxide dissolves abundantly in solutions of normal lead acetate, and forms basic salts, several of which, *e.g.* $Pb(C_2O_3H)_2 + H_2O$, have been prepared in the solid state. The solutions are called *vinegar of lead*, and are employed in medicine and as a reagent in the laboratory. They contain appreciable amounts of hydroxidion, for they react alkaline to vegetable colours.

656. **Lead Carbonate,** $PbCO_3$, can be obtained as a white precipitate from solutions in which the ions $Pb^{..}$ and CO_3 come together. Like magnesium, lead has, although in a less pronounced degree, the tendency to form basic carbonates. In nature the normal carbonate is found in the rhombic forms of aragonite, with which it is isomorphous, and is called *white lead* or *cerussite*.

White lead, the white pigment most largely employed, is a mixture of various basic carbonates. It is obtained by allowing carbon dioxide to act on lead oxide; to facilitate the reaction, acetic acid is generally used as an auxiliary substance. According to the older Dutch process, spirally rolled lead plates were placed in pots in which there was a little vinegar, and were covered with dung or spent tanner's bark, which yields the carbon dioxide by its slow oxidation in the air. In these circumstances the lead plates become covered with a layer of basic carbonate which is shaken off from time to time. At present it is usual to triturate litharge with some lead acetate and water, and to pass carbon dioxide (obtained by heating limestone) over the mixture. Further, a solution of basic acetate can be prepared from lead acetate and litharge, and this be decomposed with carbon dioxide. In this way normal carbonate is precipitated, while acetic acid, along with some lead acetate, is left in solution. The liquid is again used to dissolve lead oxide, and so on. As can be seen, the same reactions which here occur separately took place also in the first process side by side.

Lead acetate here plays the rôle of a catalyser by accelerating the combination of carbon dioxide and lead oxide, a combination which would take place without its presence, only too slowly for manufacturing purposes. In the present case the cause of the acceleration can be recognised to some extent, since by means of the acetic acid the lead oxide is converted into the dissolved condition in which it will more readily unite with the carbon dioxide.

In other words, the velocity of the action of acetic acid on lead oxide, and the precipitation of the carbonate by carbon dioxide, are together much greater than the velocity of direct combination of lead oxide with carbon dioxide. It is probable that it will be possible to attribute many cases of catalytic action to such causes.

* The characteristic of this explanation is that in place of the direct reaction, a series of intermediate reactions occur, which lead to the same final result as the direct reaction. *If these intermediate reactions occur more rapidly* than the direct reaction, the explanation of the catalytic accelerating action of the intermediate substance is given.

through overlooking the most essential part of this explanation, however, one has become accustomed to see an "explanation" of catalytic accelerations in the mere *possibility* of such intermediate reactions, without thinking of the necessity of proving that these intermediate reactions must proceed more rapidly than the direct reaction, if the entire process is to be accelerated.

657. **Lead Sulphide.**—From solutions containing plumbion, sulphuretted hydrogen, even in the presence of hydrion (if this is not too concentrated), precipitates brown-black lead sulphide. Concentrated acid prevents the precipitation, or re dissolves the precipitated sulphide. We are again dealing here with one of the equilibria which have been repeatedly discussed, and which in this case is characterised by a very slight solubility of the sulphide, and therefore a considerable lack of sensitiveness to hydrion.

This solubility is so small that even the small amount of plumbion contained in the complex salts is sufficient to exceed the solubility product on passing in sulphuretted hydrogen. For this reason all lead salts, even the complex ones, are precipitated by sulphuretted hydrogen.

Nitric acid oxidises lead sulphide to sulphate.

In nature, lead sulphide occurs in the form of regular cubes with a grey metallic lustre. It is a soft mineral of great density (7·5), which is widely distributed and is called *galena*. This is the most important lead ore.

658. **Compounds of Tetravalent Lead.**—As in the case of copper, where the salts of the monovalent type were known only in the solid state, since monocuprion immediately underwent transformation in solution, so, similarly, there is a series of lead compounds which can be referred to tetravalent plumbion, $Pb^{...}$, although this ion does not occur to any considerable extent in solution The reason of the instability of such salts is, however, to be found in another direction; it has to be sought for in the fact that the anhydride of the tetravalent hydroxide (PbO_2, $Pb(OH)_4$ $2H_2O$) is a particularly stable and difficultly soluble compound which, with the co-operation of water, is always formed in cases where the tetravalent ion $Pb^{...}$ might be expected. The hydrolytic reaction, $Pb^{...} + 2H_2O = PbO_2 + 4H^{.}$, therefore takes place, i.e. lead peroxide and free acid are formed

Lead peroxide, PbO_2, is a brown substance which has, in the crystalline condition, an almost metallic lustre; it is practically insoluble in water, and is always formed when lead compounds are subjected to powerful oxidising actions. It is generally prepared by the action of bleaching powder on lead chloride in alkaline solution; it is used in considerable quantities as an oxidising agent in the chemical industries.

On being carefully heated in the air lead oxide also undergoes oxidation not, however, to the peroxide, but to a compound of that with lead oxide; $2PbO + PbO_2 = Pb_3O_4$. The product is a powder of

a bright red colour, which has been known for a long time, and employed as a pigment; it is called *minium* or *red lead*.

* From this name is derived the designation *miniature* for ornamental designs on manuscripts, because of the use of this pigment (or of cinnabar, which was formerly confused with it) for that purpose. At the present day the word has another signification, which has a slight connection with the original one.

On treating minium with dilute acids which form soluble salts, *e.g.* nitric acid, lead nitrate passes into solution, and lead oxide remains behind as a brown powder: $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2$. In this way lead peroxide was formerly chiefly obtained.

Another and very important method of preparing lead peroxide by the conversion of lead salts, *e.g.* of lead sulphate in dilute sulphuric acid, by means of the electric current at the anode. By means of the current, sulphanion, SO_4'', is brought to the anode and discharged; there occurs the reaction $PbSO_4 + SO_4'' + 2H_2O = PbO_2 + 2H_2SO_4$. In accordance with what was stated above, it can be assumed that there first occurs the reaction $PbSO_4 + SO_4'' = Pb(SO_4)_2$, the sulphate of tetravalent lead being formed; this is hydrolytically dissociated by the water and passes into lead tetrahydroxide and sulphuric acid, or lead peroxide and sulphuric acid, according to the equation $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$. These reactions are of great importance for the construction of electrical *accumulators*, and will presently be considered more in detail.

If lead peroxide is treated with anhydrous or only slightly hydrated acids, with which therefore hydrolysis is excluded, the corresponding saline derivatives can be obtained. Thus, lead oxide dissolves in fuming hydrochloric acid in the cold to a deep coloured liquid from which, by the addition of ammonium chloride, a yellow ammonium salt of hydroplumbichloric acid, $(NH_4)_2PbCl_6$ is obtained; on decomposing this with concentrated sulphuric acid, the acid H_2PbCl_6 is formed which immediately decomposes into hydrochloric acid and lead tetrachloride, $PbCl_4$. The tetrachloride is found to be a yellow liquid which does not solidify till — 15°, and which readily decomposes into lead chloride and chlorine. When dissolved in much water it undergoes the above-mentioned hydrolytic dissociation into hydrochloric acid and lead peroxide: $PbCl_4 + 2H_2O = PbO_2 + 4HCl$.

The sulphate and acetate of tetravalent lead can also be prepared under suitable conditions; they are yellow salts which are coloured brown by water owing to the separation of peroxide.

The hypothetical lead tetrahydroxide can also act as an acid, hydrogen of the hydroxyl being split off as ion. As can be seen from the formula H_4PbO_4 and that of its first anhydride, H_2PbO_3, a tetravalent as well as a divalent acid can be derived from the hydroxide. Minium can be regarded as the lead salt of the tetra-

and, for if we replace the 4H by 2Pb we obtain $Pb_2PbO_4 = Pb_3O_4$, the formula of minium. The decomposition of the latter also by means of dilute acids speaks in favour of this view; acids first effect the formation of the free plumbic acid which decomposes into water and the anhydride, lead peroxide.

Another compound of the tetrabasic acid is that with lime, which is formed by heating a mixture of lead oxide and lime in the air, whereby oxygen is taken up. On being heated in carbon dioxide, the salt is decomposed into calcium carbonate, lead oxide, and oxygen; on being heated in the air the carbon dioxide again escapes, oxygen is again absorbed, and *calcium plumbate* is formed. A commercial method of obtaining pure oxygen has been based on these transformations.

The alkali metals, on the other hand, yield salts of the dibasic acid. Lead peroxide dissolves in a strong solution of caustic potash, and from the solution the salt $K_2PbO_3 + 3H_2O$ can be obtained in the crystalline condition. In the solution which contains excess of caustic potash, the presence of the tetravalent ion PbO_4'''' may also be assumed.

659. The Lead Accumulator.—If two lead plates, one of which is covered with lead peroxide, are placed in dilute sulphuric acid, an effective voltaic cell is obtained the potential of which is 2·0 volts, and which can yield a strong current. The chemical process taking place in this cell consists, on the one hand, of metallic lead being converted into lead sulphate, just as the zinc of the Daniell cell is converted into zinc sulphate, only that in this case the lead sulphate, on account of its difficult solubility, forms a firm layer on the electrode. On the other hand, the lead peroxide is reduced from the tetravalent stage to the divalent, and also forms lead sulphate, with the sulphuric acid present. The reaction which yields the energy for the current is therefore represented by the equation

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$
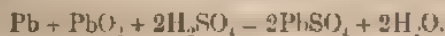
The remarkable thing about this cell is that it can be easily reversed. That is to say, if a current is passed through the cell in the opposite direction, the sulphate is at the one pole reduced to metallic lead, and at the other oxidised to lead peroxide (p. 662). The cell, therefore, again passes into its former condition, and can again yield a current.

At first sight this appears a fact of very small importance. For according to the law of the conservation of energy there can be obtained from the charged cell only as much electrical energy as was used up in the charging; in all circumstances, therefore, there is no gain, and indeed, in consideration of the unavoidable losses, there is even a profitless consumption of electrical energy. This is certainly the case; the advantage, however, which lies in the possibility of

storing comparatively large quantities of electrical energy in a small weight, and of rendering any portion of it available for use whenever desired, is so great that the above-mentioned loss is willingly accepted. Consider, for example, a factory in which large amounts of electrical energy are required from time to time, while in the intervals little is necessary : the dynamo would then have to be large enough to supply the powerful currents without being damaged, while in the intervals it would have to run empty. If, however, an *electrical accumulator* were connected with the plant, the dynamo would have to be constructed only for the average consumption, and not for the maximal, since during the time of large consumption the accumulator would yield energy, while in the intervals of small consumption the accumulator would take up the energy of the dynamo and retain it for use when required.

This result would be obtained by inserting a voltaic cell which can act in the double manner, *i.e.* which can on the one hand yield a current, and, on the other, can *store*, by means of the reverse chemical reaction, the current of opposite direction. This property is possessed by many cells, *e.g.* the Daniell, in which, by the reverse current, zinc is deposited and copper dissolved, copper sulphate therefore being formed.

Hitherto, however, the *lead accumulator* which has just been described is the only one which has proved to possess vitality, since it has the advantage of containing *only one metal*. This is rendered possible by the circumstance that the metallically conducting lead peroxide is a very strong oxidising agent, while the metallic lead acts as a (moderate) reducing agent. In the cells of the type of the Daniell, which contain two metals, one cannot, in the long run, prevent the solution of the one metal (copper) passing into that of the other (zinc), whereby instead of the indirect chemical process, which yields the current, the direct process occurs, which only yields heat, and the cell therefore no longer acts.

A *lead accumulator*, therefore, consists of two lead plates placed in dilute sulphuric acid. In order that as large an amount of electrical energy as possible may be absorbed for a given weight of the accumulator, the plates are made porous, so that the acid has as far as possible access to every part. To combine this requirement with the greatest possible durability of the plates is the real problem of the electrical accumulator. The problem is generally solved by filling up a lead grating with spongy lead, obtained by the electrical reduction of various lead compounds. Such a plate of spongy lead is then connected with a second plate, in which the spongy lead has been converted into lead peroxide by electrical oxidation. Such plates are prepared, for example, by filling in the lead grid with a mixture of lead oxide and sulphuric acid in the form of a thick paste, suspending two such plates, after the paste has solidified, in dilute sulphuric acid, and passing a

ent through it. On the one side the lead sulphate present is then
uced to metallic lead, and on the other oxidised to peroxide. The
of the transformation can be recognised in the evolution of hydro-
at the former plate and of oxygen at the latter; at the same time,
potential of the current necessary for charging rises. The accumu-
is then *charged*. When, after the charge has been withdrawn,
accumulator has to be recharged, care has to be taken that the
er peroxide plate is again used for the same transformation, as
rwise the plates will be destroyed.

As can be seen from the equation of the reaction given on p. 663,
huric acid *passes into combination* while the accumulator is in
, and is again set free when the cell is charged In the amount
lphuric acid in the accumulator, therefore, we have a measure of
condition of charging, and as the density also changes with the
unt of acid, a hydrometer floating in the liquid allows of the
dition as to charge being easily determined. This is of importance,
experience has shown that an accumulator deteriorates on stand-
for a lengthened period in the uncharged condition, because the
sulphate in the plates partially loses its chemical reactivity.

660 **Metallurgy of Lead**. For the manufacture of lead, *galena*
only ore which has to be considered in practice. This is first
ed, whereby a part of the sulphur escapes as sulphur dioxide,
e another portion remains behind in the roasted mass, the lead
hide being converted into lead sulphate. The mixture of lead
e, lead sulphate, and unchanged lead sulphide is then fused with
sion of air, whereby the following reactions occur :—

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$
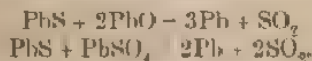
In this particular case, therefore, the unchanged lead sulphide acts
reducing agent on the oxygenated products formed, and the result
etallic lead along with sulphur dioxide.

The "work lead" thus obtained generally contains silver, to
ain which it is further treated; the processes for this will be
ussed under silver.

CHAPTER XXXIV

MERCURY

661. General—In its chemical relations mercury is most nearly allied to copper, since it forms, like it, two elementary ions, a monovalent and a divalent, which in many respects also are similar to those of copper. With cadmium it shares the tendency to form slightly dissociated halogen compounds of the divalent series.

Metallic mercury occurs free in nature, and by reason of its being liquid at medium temperatures it has attracted attention from remote times. In the older history of chemistry, while the experimental conception of a chemical element was not yet developed, mercury was regarded as the type of the *metallic character*, this found expression in the fact that mercury was regarded as a constituent of all metals. The endeavours to prepare gold and silver from base metals, which are connected with this view, had generally for the first purpose, the "fixing" of the mercury, *i.e.* making it non-volatile. For this reason, and through the discovery made about the fifteenth century of the powerful medicinal actions of the mercury preparations, the chemistry of mercury became known at an earlier period than that of most of the other metals.

During the development of the newer period of chemistry at the end of the eighteenth century mercury again played a considerable rôle. This was due, in the first place, to the chemical properties of mercury oxide. The possibility of converting the metal into its *oxide* by heating in the air, and of effecting the separation of this into metal and oxygen by more strongly heating, was of the greatest importance for the correct interpretation of the phenomena of oxidation (p. 374). On the other hand, the introduction of the *mercury pneumatic trough* for the investigation of gases at once led to the discovery of a series of hitherto unknown substances (p. 182).

Up to the present day mercury has not lost its importance for scientific investigation. Its liquid nature, fairly great chemical resistibility, considerable density, etc., assure its unceasing use for physico-chemical apparatus, of which the *thermometer* and *barometer* need

only be mentioned as the most important. Since, being a liquid metal, it is not subject to the variations which are exhibited by the solid metals in consequence of being wrought, it is employed as a standard metal for electro-chemical apparatus, and many other scientific applications could also be mentioned.

Metallic mercury has the density 13·595 at 0°. Its expansion by heat is, up to the boiling point of water, so nearly proportional to that of the gases that the mercury thermometer agrees well with the gas thermometer over this range. At 39·4°, mercury solidifies to a silver-like solid metal ; it thereby readily exhibits in a considerable degree the phenomena of supercooling (p. 120). At 358° mercury boils under the pressure of the atmosphere. Since, in many measurements, the vapour pressure of mercury at comparatively low temperatures also comes into account, we give the following table of vapour pressures :

0°	.	0·00002 cm.	158	.	0·29 cm.
20	.	0·00013 ,,	200°	.	1·82 ,,
40	.	0·0007 ,,	250°	.	7·58 ,,
60	.	0·0028 ,,	300	.	24·2 ,,
80	.	0·0093 ,,	350°	. .	66·3 ,,
100	. .	0·0280 ,,			

From this it is seen that up to 100 the vapour pressure is small, viz. less than 1 mm.

In the air mercury behaves in general as a "noble" metal, i.e. it does not oxidise spontaneously. This is not, however, in all strictness the case, for if it is maintained for a lengthened period at about 300 , it slowly becomes covered with red crystals of mercury oxide. Water, standing in contact with mercury, assumes poisonous properties. Whether this is due to the solution of a trace of oxide formed, or to the solution of metal in water, has not yet been determined.[1]

The *combining weight* of mercury has been found by analysis of the oxide and sulphide to be Hg = 200·0. The vapour density shows the molar weight to be 200 ; the two are therefore equal. On account of its low boiling point mercury was the first metal in the case of which this remarkable relation was established (p. 477).

Pure mercury does not wet glass ; if, however, it contains foreign metals dissolved in it, it becomes covered with a film of oxide, the effect of which is that the metal no longer flows over glass and other surfaces in round drops, but "leaves a tail." This is a very sensitive test of the purity of the metal.

* In order to purify mercury, a task which is constantly occurring

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[1] That metallic mercury can dissolve in water must be regarded as indubitable. For all gases dissolve in water ; since mercury has an appreciable, although small , vapour pressure even at room temperature, its vapour must also be soluble in water. There is, however, no difference between a solution of liquid and one of vapour as mercury, since in the case of a solution only the existing state is of importance and not the former states of its components.

... mercury, it is shaken with dilute sulphuric acid, to which from ... time some drops of potassium dichromate are added; it is then washed with a large quantity of water and dried by gently heating it. In this way considerable impurities can be quickly removed. The fairly pure metal is allowed to flow in small drops through the apparatus shown in Fig. 120, which is filled with a dilute acid solution of mercurous nitrate (*vide infra*). These methods depend on the fact that the oxidising agents supposed oxidise the contaminating metals rather than the mercury; in order that the object may be attained fine division is necessary.

662. **Mercury Ions.**—Mercury forms two elementary ions: monomercurion, Hg', and dimercurion, Hg. In its properties the former is allied to monocuprion and argention; the latter does not exhibit any very close relations to other metals. In comparatively concentrated solutions monomercurion, perhaps, occurs as the divalent double ion of the formula Hg_2; in very dilute solutions, as monovalent Hg. For the sake of clearness, and until the corresponding relations have been explained in the case of the other monovalent ... the heavy metals, we shall use the simple method of writing ... especially as it does not conflict with any experiment ... discussed here.

... is formed when salts of mercury are prepared ... an excess of metallic mercury. The most convenient ... for mercury is dilute nitric acid; if too great a concentration ... and too high a temperature are avoided, mercurous ... formed with evolution of nitric oxide (p. 326). If, owing ... just mentioned, mercuric nitrate has been formed, it ... allow the solution to stand for some time over metallic ... order to again convert it into mercurous salt. The ... Hg = Hg + 2Hg then takes place almost completely ... essence of metallic mercury, however, monomercurion ... converted to dimercurion

... actions of the two ions cannot be distinguished by their ... since they are both colourless. Their compounds, however ... the same anion have frequently very different solubility ... be distinguished by this means

... ions are violent *poisons* both for the higher and the lower ... Since, however, monomercurion forms a very difficultly ... compound with the chloridion occurring everywhere in the ... with its concentration and therefore its action is ... exceedingly small values, mercury poisoning occurs, as ... almost exclusively by means of dimercurion.

663. **Mercurous Compounds.** From the solutions of mercurous salts, black *mercurous oxide*, Hg_2O, is precipitated by bases. The mercurous hydroxide, the formation of which might be expected, is so unstable that it has not been possible to detect it with certainty ; on formation it apparently passes immediately into its anhydride. Mercurous oxide is a black, unstable powder which on being kept for some time is converted into mercuric oxide and metallic mercury : $Hg_2O = HgO + Hg$; in sunlight the conversion is rapid.

The basic properties of this oxide are only feebly developed, for the mercurous salts, so far as they are soluble in water, undergo hydrolysis with formation of precipitate of difficultly soluble basic salts. In order to obtain clear solutions excess of free acid must be added.

This holds, for example, in the case of *mercurous nitrate*, $HgNO_3$, which is readily obtained by dissolving mercury in dilute nitric acid. In the cold the salt crystallises from the solution containing excess of acid ; on attempting, however, to re-dissolve it in water, a white precipitate of basic nitrate is deposited, the amount of which is all the greater the greater the amount of water compared with that of the salt. The solution can be again made clear by the addition of nitric acid, and there is a definite concentration of free acid, varying with the temperature, at which no decomposition of the salt occurs.

664. **Mercurous Sulphate**, Hg_2SO_4, is a salt, very difficultly soluble in water, which is formed by warming mercury with concentrated sulphuric acid. Half of the sulphuric acid then acts as an oxidising agent, and passes into sulphur dioxide and water ; the other half of the acid yields mercurous sulphate, which is deposited as a white, coarsely crystalline powder. If the excess of sulphuric acid is removed by washing with water, hydrolysis commences after the main portion of the acid has been removed, and the salt becomes dark in colour.

Mercurous sulphate is used as the initial substance in the preparation of other mercury compounds, and for the construction of electrical standard cells.

Such standard cells serve the purpose of furnishing at all times a definite value of electrical potential for the purposes of measurement. The most largely employed of these cells is represented in Fig. 121. In the one limb there is contained mercury covered with mercurous sulphate, and in the other there is a 12 per cent mixture of cadmium and mercury ; the remaining space is occupied with a saturated solution of cadmium sulphate, to which some crystallised cadmium sulphate has been added. The potential of such a cell amounts to 1·0186 volt ; by using fairly pure substances, the same

Fig. 121.

... always obtained to within a ten-thousandth of its value
... ... slightly with the temperature.

Mercurous Chloride, HgCl, is a white salt, soluble with
... ... in water, and has long been employed in med...
... ... By reason of its small solubility it passes
... ... the system, and therefore exhibits correspondingly
... ... Its application in medicine depends on this.

... is obtained on bringing together a soluble mercurous salt
... ... that mercurous salts are precipitated not only by
... ... chlorides, but also just as completely by hydro-
... ... This behaviour could be foreseen, for the solubility of
... ... salts in acids depends, indeed, on the fact that their
... ... undissociated compounds with the hydrion of the
... ... so that the concentration of the anion is diminished, and
... ... product thereby not attained. In the present case this
... ... because the anion of calomel, viz. chloridion, is that of
... ... strongest acids, and is therefore not converted to any con-
... ... extent into the undissociated condition even by the addition
... ... For this reason the concentration product of a calomel
... ... also remains essentially unchanged on the addition of a strong
... ... more passes into solution.

... treating calomel with a *concentrated* solution of sodium chloride
... ... acid, however, a quite appreciable amount of it passes
... ... at the same time some mercury is deposited. This
... ... be explained in the case of the iodine compound, in which
... ... more distinct.

Mercurous sulphate also is converted into calomel on being treated
... a solution of sodium chloride or hydrochloric acid, because the
... ... more difficultly soluble. As a rule, however, it is obtained
... ... sulphate by subliming it with common salt, whereby the
... ... obtained in semi-transparent crystalline masses with a
... ... lustre on account of its high index of refraction. Since
... ... more or less mercuric chloride is mixed with it, calomel,
... ... be used for medicinal purposes, must be previously care-
... ... with water in order to remove the very poisonous
... ... chloride.

... readily volatilises, and its vapour density was therefore
... ... This yields the molar weight 235, corresponding
... ... formula HgCl. Since mercury was regarded as being
... ... this result stood in conflict with a former, specially
... ... according to which the different elements possess
... ... valency; the double formula Hg_2Cl_2, however,
... ... into agreement with the divalency of mercury,
... ... recombination ClHg—HgCl. A lively discussion there-
... ... whether the vapour of calomel is uniform or has
... ... mercuric chloride and mercury, according to the

equation $Hg_2Cl_2 = HgCl_2 + Hg$. An unequivocal decision of this point, supported by numerical data, has not yet been effected.

Mercurous bromide and iodide are similar to calomel. The iodide is a greenish powder, which is most easily obtained by rubbing iodine and mercury together in the proportions of their combining weights, and which decomposes with extreme readiness into mercuric iodide and free mercury.

666. **Mercuric Salts** are obtained from the mercurous compounds by subjecting these to oxidising actions. Thus, *mercuric nitrate*, $Hg(NO_3)_2$ is formed on dissolving mercury in concentrated and warm nitric acid, and can be obtained in colourless crystals on evaporating the solution. In the same way mercurous sulphate, on being heated with an excess of sulphuric acid, passes into mercuric sulphate with renewed evolution of sulphur dioxide: $Hg_2SO_4 + H_2SO_4 = 2HgSO_4 + SO_2 + H_2O$.

The mercuric salts exhibit the property of hydrolysis in a much higher degree than those of the mercurous series. Since in this case the basic salts are characterised by a yellow colour, the occurrence of the decomposition can be readily recognised. Nevertheless, a number of salts of the mercuric type are known, which can be dissolved in water without sign of decomposition: this is due to special properties, which will be discussed immediately.

Mercuric oxide, HgO, is obtained from the mercuric salts by means of soluble bases. The hydroxide is not known; it may therefore be again assumed that it is indeed first formed, but that it immediately passes into its anhydride.

Mercuric oxide is a yellow to red powder, the colour of which depends on the fineness of its division. If it is precipitated from cold solutions it appears yellow; when precipitated hot an orange-coloured precipitate is formed. It is obtained as a red crystalline powder by heating mercurous or mercuric nitrate to a moderate temperature; nitrogen peroxide and oxygen escape (cf. p. 657), and mercuric oxide remains behind. The decomposition can easily be made complete without the temperature being reached at which the oxide decomposes into the metal and oxygen.

As has been repeatedly mentioned, mercuric oxide is also produced directly from mercury and oxygen by allowing the two to act on one another at about 300. The reaction is, however, very slow. In this case a condition of equilibrium, depending on the temperature, is established between mercury, oxygen, and mercuric oxide. According to the temperature and pressure of the oxygen the reaction can be made to take place in one or other direction.

The preparation of *mercuric nitrate* has been already given. The basic nitrate which is precipitated from the salts by water has the composition $Hg_2(NO_3)_2(OH)_4$. It readily dissolves in hydrochloric acid, forming a clear solution.

The same holds for *mercuric sulphate*, $HgSO_4$. The basic salt which is obtained as a yellow crystalline precipitate on treating the normal salt with water, has a corresponding composition $Hg_3SO_6(OH)_4$, and under the name "*turpeth mineral*" is applied in medicine. Recently, mercuric sulphate has become of importance as a catalyser for the oxidation of organic substances by hot sulphuric acid, both for analytical and technical purposes (oxidation of naphthalene to phthalic acid for the preparation of artificial indigo).

The behaviour of the *halogen compounds* is in marked contrast to that of the mercuric salts of the oxyacids. So far as they are soluble, they dissolve in water without appreciable hydrolysis, and exhibit nothing of the ready decomposability of the above salts.

The explanation is found on determining the electrical conductivity of the solutions of these substances. This is found to be very slight, and it follows from this that we are here dealing with salts which, unlike the preponderating majority of such substances, are not greatly dissociated into ions; they can exhibit the reactions of the ions, therefore, only in a very limited degree.

The salt which is most dissociated is mercuric chloride, $HgCl_2$. This chlorine compound of mercury has also been known for a very long time. On account of its poisonous properties and its method of preparation (by the sublimation of mercuric salts, especially the sulphate, with sodium chloride) it is called corrosive sublimate.

Mercuric chloride is a colourless, crystalline salt, which is moderately soluble in water; it has a considerable density (7.2), and its solutions have been found to be a very violent poison for higher as well as lower organisms. It is therefore extensively used in medicine as a disinfectant, *i.e.* for the purpose of killing the spores of harmful schizomycetes, and such like, and its use is limited only by the fact that it is also a powerful poison for the human organism. Small quantities of it exercise a specific, medicinal action.

At 265° mercuric chloride melts, and boils at 307°, so that it can be readily volatilised, and thereby purified. Its vapour density yields the molar weight 271, corresponding to the formula $HgCl_2$.

* The solutions of mercuric chloride are fairly easily reduced to calomel. Of these reductions, that with *oxalic acid* (p. 415) is of particular interest, as it takes place with measurable velocity only in light, while in the darkness it remains practically at a standstill. This reaction has therefore been used as a means of measuring the chemical action of light or as a chemical photometer. It is represented by the equation $2HgCl_2 + C_2O_4H_2 = 2HgCl + 2CO_2 + 2HCl$. Carbon dioxide and hydrochloric acid are therefore formed in the reaction; to counteract the action of the latter one of the salts of oxalic acid, e.g. ammonium oxalate, is used instead of the free acid. The indications of this photometer are also only individual (p. 592).

From its solutions *mercuric oxide* is precipitated by soluble, strong

ises, but on quantitative investigation it is found that the amount of oxide precipitated never corresponds to the amount of base taken, but is less. Conversely mercuric oxide dissolves in solutions of other chlorides, and liquids are produced with a strongly alkaline reaction. This is due to the fact that the solution of mercuric chloride contains very little dimercurion. On adding a base, i.e. hydroxidion, there must be a certain, finite concentration of the latter before the solubility product of the mercuric oxide is reached and that substance precipitated. On the other hand, when chloridion is added to an aqueous solution of mercuric oxide (in which the presence of dimercurion and hydroxidion must be assumed), the greater part of the mercurion present is converted into undissociated mercuric chloride, and more mercuric oxide must pass into solution in order that the solubility product may be again established. This process is repeated, and when equilibrium is finally reached there is an appreciable amount of hydroxidion, from the mercuric oxide, present in the solution.

Mercuric chloride is extremely stable to concentrated sulphuric acid, and even on heating no evolution of hydrogen chloride occurs. Nor is it acted on by concentrated nitric acid, which attacks all other saline chlorides with evolution of chlorine or nitrosyl chloride (p. 338). The behaviour in both cases is due to the very slight electrolytic dissociation of mercuric chloride.

Mercuric chloride crystallises along with the alkali chlorides, forming compounds which appear to occupy a position intermediate between the ordinary double salts, the components of which exist side by side in solution, and the complex salts, the ions of which are formed by the ion of the one salt with the ion of the other, that is to say, the salts partly exist side by side in solution, and are partly combined in the above complex compounds, and the relative quantities of the two depend on the temperature and the concentration.

Strictly speaking, such a view holds for all double salts and complex salts, and the two are distinguished from one another only by the fact that the one or the other greatly predominates. In the case of the above mercury compounds we have apparently the case, which otherwise does not frequently occur, that the two portions are present in about equal amounts.

The complex salts whose presence can here be assumed, are the alkali salts of the mercurichloride ions $HgCl_3'$ and H_2Cl_4. From the solutions of the mixed single salts compounds of the one or other type, as $KHgCl_3$ and K_2HgCl_4, are obtained, according to the concentration and the temperature, and we must therefore regard both as being present together in solution. If for any reason one or other of these compounds separates out, the equilibrium in the solution is disturbed; the compound is again formed at the expense of the substance present, and so on. A more thorough investigation of the conditions of equilibrium has still to be carried out.

2 X

...tic substance, and 126° is the transition temperature which separates ...two regions of stability from one another (p. 257).

' If in any way, however, solid mercuric iodide is caused to form ...a lower temperature, it is always the yellow form that first appears. ...is is one of the most striking examples of the rule which has often ...en mentioned that the unstable forms appear first. This can be ...ily observed by precipitating mercuric chloride with a solution of ...tassium iodide. A bright yellow precipitate is first formed, which in ...few moments changes into the red one. The yellow form maintains ...existence longer when formed by the precipitation of an alcoholic ...ution of the salt with water. In consequence of its very fine state ...division it is very light yellow, almost white, in colour. The ...version into the stable red form is greatly accelerated by light. ...en exposed to sunlight the vessel with the light yellow pre...itate becomes red in a few minutes on the side turned towards the ...ht.

' Further, when the red salt is volatilised, the vapour always ...ndenses on the colder portions in the yellow form. This occurs, no ...tter whether the vapour has been generated from the red or the ...llow salt, which shows that the distinction between the solid forms ...es not exist in the vapour.

Mercuric iodide is a very stable compound, which is scarcely attacked ...dilute solutions of the ordinary reagents. This is due to the fact ...at it is even less dissociated into its ions than mercuric chloride ... On the other hand, it is formed with extreme ease from its ...nstituents.

Mercuric iodide forms very stable complex compounds with the ...dine compounds of the other metals. These will be described ...ter.

The behaviour of *mercuric fluoride* is in striking contrast with the ...reat stability of mercuric chloride, bromide, and iodide. Mercuric ...xide it is true, dissolves in excess of hydrofluoric acid, but on diluting ...e solution with water a basic salt of a yellow colour is deposited, and ...this is treated with further quantities of water pure mercuric oxide ...mains behind free from fluorine compounds. This is a behaviour ...culiar to the oxy-salts of mercury, and shows the considerable ...viation of fluorine from the other halogens (p. 242).

929 **Mercuric Sulphide.**—While a sulphur compound corre...ponding to mercurous oxide is not known, the compound HgS, cor...ponding to mercuric oxide, is a very stable substance which is readily ...ormed, occurs naturally, and has long been known.

' If the solution of a *mercurous* salt is precipitated with sulphur...tted hydrogen, a black precipitate is indeed formed ; but on investiga...on this is found to be a mixture of mercuric sulphide and metallic ...ercury. It can be assumed that the mercurous sulphide first formed ...composes into these two substances : $Hg_2S = HgS + Hg$.

Mercuric sulphide is obtained as a black powder by triturating the two components together. It is also obtained by the precipitation of mercuric compounds with sulphuretted hydrogen. In this case it is indifferent whether the solution reacts acid or neutral, since mercuric sulphide is extremely difficultly soluble, and its precipitation is therefore not appreciably affected by acids. From the other metallic sulphides it is distinguished by the fact that it does not have the least tendency to oxidise in the air. It is a much more stable compound than mercuric sulphate, which could be produced by its oxidation.

In nature mercuric sulphide occurs in comparatively large quantities. It constitutes the most important ore of mercury, and is called cinnabar. Pure cinnabar crystallises in red-grey, hexagonal masses with metallic lustre, and on being ground yields a powder of a fine red colour. It is another form of mercuric sulphide; the black product may be regarded as amorphous.

From the fact that the black form was first produced in the formation of mercuric sulphide, it can be concluded that it is the less stable, and the red crystalline form the more stable variety. This follows from the spontaneous transformation of the former into the latter. If a solution of alkali sulphide (in which mercuric sulphide is somewhat soluble) is poured over the black mercuric sulphide, red spots are formed after some time in the black mass, and these continue to grow until the whole mass has become red, i.e. has become converted into the crystalline form.

The more stable red form can also be obtained by the slow sublimation of the black sulphide.

* Being the less stable form, the black mercuric sulphide must be more soluble in all solvents than the red. If, therefore, the liquid is saturated in respect of the black form, it is supersaturated in respect of the less soluble red form, and if any of the red form is present or is produced, a further quantity of the red sulphide must there separate out. The solution thereby becomes unsaturated in respect of the black form, and a further portion of this is dissolved. In this way precipitation and solution are repeated until the unstable form has completely disappeared. Transformations of this kind are therefore generally accelerated by solvents, since these act as intermediaries, whereas otherwise only those portions of the two forms which are in direct contact can influence one another.

On account of its fine colour cinnabar is used as a pigment. It is, however, not very stable to light. The two forms of mercuric sulphide are not appreciably soluble in dilute acids, and nitric acid also is without action on them. They dissolve, however, in aqua regia or in reagents which evolve free chlorine. This behaviour is due to the slight stability of the oxygen salts of mercury and the great stability of the halogen compounds. This is made use of for the analytical

coloured substance, which is not metallic silver, as it does not dissolve in dilute nitric acid. It has recently been shown that silver sub-chloride, Ag_2Cl or Ag_4Cl_2, is here formed, which can be again con-verted into silver chloride by means of chlorine. Under the influence of the light, a decomposition of the silver chloride into sub-chloride and free chlorine occurs; equilibrium is established when the concen-tration of the chlorine in contact with these two substances has reached a definite value. This value is all the greater the stronger the light, and becomes vanishingly small in darkness. In the case of this equili-brium, therefore, the strength of the light plays a rôle similar to that of temperature in the decomposition of calcium carbonate by heat.

If the decomposition is carried out under such conditions that the chlorine can pass into other compounds, it is unlimited, and occurs in proportion to the strength of the light and to the time. The use of silver chloride for making copies of photographic negatives depends on this. The binding of the liberated chlorine is effected by the organic compounds which are always present.

* The action of light on silver chloride takes place more slowly than in the case of the other halogen compounds of silver. It is there-fore not used for taking photographs directly, as it is not sufficiently sensitive for this purpose.

* In the case of silver chloride, it is the blue and the violet rays that exhibit the greatest chemical activity. The region of active rays, however, can be shifted to a considerable extent by the presence of other substances.

Silver chloride is the form in which chlorine is identified and estimated; the estimation is effected by adding excess of silver nitrate to the solution in question, and filtering off and weighing the silver chloride produced.

Conversely, silver can be estimated in the form of silver chloride. This method has been elaborated chiefly for the estimation of this metal in bar-silver in governmental mints. The method is carried out by dissolving a weighed amount of the metal, and adding a solu-tion of sodium chloride of known strength until a precipitate just ceases to be produced. The property of silver chloride of cohering together renders this method possible; for a solution which still con-tains an excess of silver chloride can be made quite clear by shaking, because the silver chloride forms into flakes, which in a few moments sink down and leave a clear liquid. It is easy to see if a turbidity is produced in this on the addition of sodium chloride. This is histori-cally the first case in which the method of volumetric analysis (p. 199) was elaborated.

Silver chloride accumulates from many chemical analyses; further, it is a form of compound into which other silver compounds can be easily converted, and in which silver can be separated from other sub-stances. The need often arises, therefore, of again preparing metallic

of obtaining cyanogen gas (p. 418). In this process a portion of the cyanogen always separates out in the polymerised condition as a brown powder of paracyanogen.

If the solution of mercuric cyanide is mixed with that of an alkali cyanide, a considerable evolution of heat occurs, which indicates the formation of a new compound. This can also be obtained in the solid state; the potassium compound has the composition $K_2Hg(CN)_4$, and is the potassium salt of a mercuricyanidion $Hg(CN)_4''$, which is similar in composition to the nickelcyanidion (p. 627).

The corresponding acid $H_2Hg(CN)_4$ is not very stable, but decomposes readily into mercuric cyanide and hydrocyanic acid.

671. Complex Compounds of Mercury. As might be expected from the slight dissociation of the halogen compounds of mercury this metal has a great tendency to form complex compounds, the aqueous solutions of which contain dimercurion only in extremely small amount, and in which mercury forms a component of more complex ions or salts. Such complex compounds are met with, on the one hand, in the case of the halogen derivatives; on the other hand, sulphur and nitrogen also have the power of forming many such compounds with mercury. On account of the large number of such substances these cannot be treated exhaustively here, and the characterisation of the most important types must suffice.

In the first place, the three heavier halogens form such complex compounds, the stability of which increases with the combining weight of the halogens. The most important type represented here is that of the halogenmercuric ion HgA_4, where A denotes the halogen. It will be sufficient if we describe the relations in the case of the iodine compound, which is the most stable, and which, on account of the difficult solubility of mercuric iodide, gives rise to the most readily understood phenomena (cf. p. 671).

Mercuric iodide readily dissolves in aqueous solutions containing iodidion, and it does so all the more abundantly the more concentrated the solutions. On dilution, mercuric iodide is precipitated, but there always remains in the solution rather more of it than corresponds to the relation $HgI_2 . 2I'$. The solutions are pale yellow in colour, exhibit none of the reactions of mercury, and partly yield the corresponding salts in the solid state on evaporation, e.g. the potassium salt K_2HgI_4, they contain the complex anion HgI_4''.

No mercuric oxide is precipitated from their solutions by the addition of strong bases; on the other hand, mercuric oxide dissolves abundantly, for example, in a solution of potassium iodide, yielding a solution with a strongly alkaline reaction. In this case the reaction $4KI + HgO + H_2O = K_2HgI_4 + 2KOH$, or writing the ions, $HgO + H_2O + 4I' = HgI_4'' + 2OH'$, takes place to a large extent. Such an alkaline solution of *potassium mercuric iodide* is used under the name of "Nessler's reagent" for the detection of small traces of ammonia.

picture is therefore produced on the plate in which the bright parts contain a dense, the dark parts a slight or no precipitate. If, after sufficient development, the remaining silver bromide is removed by dissolving in sodium thiosulphate, a "negative" is obtained, i.e. a picture with opaque high lights and transparent shadows.

On what the property of the illuminated silver bromide of being more quickly reduced depends, is still somewhat a matter of dispute. By far the most probable view is that under the action of the light an incipient reduction occurs, and therefore a picture of silver sub-bromide exists even in the undeveloped plate, and is invisible only on account of its small density. This is confirmed by the fact that by treatment with free bromine or any other oxidising agent, the "latent" picture is made to disappear, i.e. its power of being developed is destroyed.

The development, now, depends on the fact that a supersaturated solution of silver is produced by the reducing liquid, from which metal is deposited at those parts where there are already nuclei of silver present (p. 492). These are presumably formed by the developer from the readily reducible sub-bromide.

682. Silver Iodide, AgI, is also immediately formed when its ions come together, and of the three halogen compounds of silver it is by far the most difficultly soluble. It is a yellow powder which is dissolved only in traces, even in ammonia, and requires comparatively large amounts of sodium thiosulphate for its solution. It readily dissolves, however, in potassium cyanide. This proves that the concentration of argention is relatively greatest in its complex ammonia compound, is smaller in the thiosulphate compound, and is smallest in the cyanogen compound.

Silver iodide was formerly chiefly used as photographic substance, and this both for the method of Daguerre (the first real photographic method) and for the later *collodium process* which is still in use for particular purposes.

The method of Daguerre depends on the fact that the "development" of an exposed silver iodide plate is accomplished by exposing the illuminated plate to the vapours of mercury.[1] A plate of silver

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[1] The history of the discovery of this method is instructive; it is related as follows. Daguerre at first attempted to utilise directly the blackening of silver iodide in light, and he directed his efforts to preparing the layer in such a way that the blackening should occur as quickly as possible. On one occasion he had just begun to take a picture but had had to interrupt his work, and since no blackening had as yet made its appearance on the plate, he intended to use it for a further experiment, and placed it therefore in a dark press. Next day he found the picture on the plate. He was soon to assure himself that a picture was always produced when he placed a plate, after short exposure, in the press, but was unaware as to which of the objects present in the press produced this effect. He therefore removed these objects one after the other, but still always obtained pictures even when the cupboard was quite empty. In other cupboards under the same conditions no picture was produced. Finally he discovered some mercury which had been spilt in the joints of the wood, and on making the appropriate experiment, he found that the picture was developed by being left over metallic mercury.

ammonium is replaced by mercury, only that in this case one combining weight of mercury, on account of its divalency, replaces two combining weights of hydrogen. From these considerations we obtain, in the first instance, the following cations :

Dimercurammonion	Hg_2N
Mercurammonion	HgH_2N
Mercurdiammonion . .	HgH_4N_2

In the case of dimercurammonion, all the hydrogen of the ammonium is replaced by mercury; in mercurammonion, only the half ; and mercurdiammonion, finally, corresponds to two combining weights of ammonium, which have together lost two hydrogens, these having been replaced by one combining weight of mercury.

The hydroxide corresponding to dimercurammonion is obtained on allowing finely divided mercuric oxide to stand under concentrated ammonia solution. Without apparently any great change taking place —the colour only becomes somewhat lighter—there occurs the reaction $2HgO + NH_3 = Hg_2N(OH) + H_2O$. The hydroxide produced is almost insoluble in water, explodes on being heated, and forms with most of the acids yellow to brown coloured salts, which are also almost insoluble. Of these, the *iodide* is the best known, as it is formed as a brown precipitate when ammonia is added to an alkaline solution of potassium mercuric iodide (p. 678). Even extremely small amounts of ammonia can in this way be detected by the yellow brown coloration of the liquid, and this reaction, called by the name of its discoverer the *Nessler reaction*, is used both for the detection and the approximate estimation of very small amounts of ammonia, such as occur for example, in the ordinary water-supply. For quantitative purposes the coloration which is produced by the water to be investigated, is compared with a series of colours produced by known, graduated amounts of ammonia (in the form of very dilute solution of ammonium chloride) under the same conditions.

Of the two other types, the chlorine compounds are the best known ; they are formed by precipitating solutions of mercuric chloride under different conditions with ammonia. If a solution of the mercuric salt is added in the cold to excess of dilute ammonia, *mercuram-monium chloride* HgH_2NCl is precipitated as a white substance which, on being heated, sublimes with decomposition without previous melting. The sublimate consists chiefly of calomel, while a mixture of nitrogen and ammonia escapes ; the latter generally blackens the sublimate of calomel $6HgH_2NCl = 6HgCl + 4NH_3 + N_2$. This compound was formerly used as a medicament, and was called *infusible precipitate*.

If the ammonia is allowed to act on the mercuric chloride in hot solution in the presence of much ammonium chloride, a liquid is obtained which is clear when hot, and which on cooling deposits small crystals of a white salt ; this is the chloride of *mercurdiammonium*, and

therefore, the formula $HgH_6N_2Cl_2$. This formula can be resolved
to mercuric chloride plus ammonia, $HgCl_2 + 2NH_3$; the complex
nature of the salt is, however, seen from the fact that it does not
evolve any ammonia with a solution of caustic potash, and is only
composed by this reagent on being strongly heated. Since on being
heated the salt melts to a clear yellowish liquid, it was called *fusible
precipitate* to distinguish it from mercurammonium chloride or infusible
precipitate.

Besides the above compounds, there are others belonging to the
ammonia series which, however, will not be mentioned here, as they
have not been investigated in sufficient detail.

673 Other Complex Nitrogen Compounds —Another complex
mercury salt containing nitrogen which must be mentioned is potassium
mercurinitrite, $K_2Hg(NO_2)_4$, which is obtained by dissolving mercuric
oxide in a solution of potassium nitrite (whereby there is an evolution
of heat), and destroying the basic reaction with acetic acid. From
this solution a finely crystalline, bright yellow salt is obtained, which
has the above composition, and is readily soluble in water. The
solution is neutral, and can be boiled without decomposition; it does
not exhibit, therefore, any of the hydrolysis of the normal mercuric
salts.

Further, mercury enters extremely readily into organic compounds
containing the *imide* group, NH The substances produced do not
exhibit the reactions of mercury, and therefore contain this element in
complex Since they belong to organic chemistry, however, the
statement that they are characteristic of mercury must suffice here.
Compounds, further, containing the amide group, NH_2, show these
properties, but in a less degree than the imido compounds.

To this class also belong the cyanogen compounds, concerning
which the necessary information has already been given (p. 678).

674 Complex Sulphur Compounds. —The tendency of the two
elements, sulphur and mercury, to combine, which is disclosed in the
great stability of mercuric sulphide, asserts itself also in the formation
of complex compounds on allowing the lower oxyacids of sulphur and
mercury compounds to come together. Thus, mercuric oxide dissolves
in the normal alkali salts of sulphurous acid and thiosulphuric acid,
with great rise of temperature and production of an alkaline reaction;
in these two salts most of the other difficultly soluble salts of mercury
are also readily soluble. The cause in both cases is to be found in
the disappearance of dimercurion, owing to the formation of a complex
compound.

By dissolving mercuric oxide in potassium sulphite and crystallis-
ing, there is obtained the salt $K_2Hg(SO_3)_2$, which is the potassium salt
of mercurisulphoston, $Hg(SO_3)_2$ potassium hydroxide is also formed
at the same time, and remains in the mother liquor. The exist-
ence of this salt in the strongly alkaline liquid is sufficient to show

... the ....ation of the complex salt, however, the concentration ... . is so small that this direct reaction does not occur to ... . extent, and the separation of silver takes place only ... . the electric current.

... . considering the formula of potassium argenticyanide, ... , it is seen that the product of electrolysis should be, ... hand, potassium, and, on the other, the discharged anion, ... Instead of this silver appears at the cathode, and the anode .... silver) dissolves. We are dealing in both cases with .... reactions.

... The separation of potassium at the cathode would require ... . potential than that of argention, in spite of the small .... of the latter. Thus the conduction of the current in ... . it is true, is effected as far as the cathode by potassium. ... . of electricity at the cathode, however, occurs not by ... ... of potassium, but by that of the argention. Formally ... . can also be expressed by saying that potassium is in ... . but at once undergoes double decomposition with the ... . with separation of silver, according to the equation .... + K = Ag + 2KCN. Silver and potassium cyanide are ... . formed.

... At the anode the ion Ag(CN)₂' is discharged, and acts on the .... silver, silver cyanide being formed according to the equation ... AgCN₂ = 2AgCN. This is at once dissolved to potassium ... cyanide by the excess of potassium cyanide present, and the .... of the latter is again made good by the potassium cyanide ..... is formed at the cathode. It is necessary, however, to keep the ... in movement, as otherwise the potassium cyanide would accumu-... at the cathode, and would hinder the separation of the silver, ... at the anode a deposition of silver cyanide would immediately .... on account of a lack of potassium cyanide.

... **Complex Salts in the Voltaic Cell.**— When voltaic cells ... constructed with silver in solutions of ordinary silver salts, it is ...... that silver is almost at the end of the potential series, which ... . that the formation of the ion takes place with greater difficulty ... in the case of most of the other metals, and conversely, the ... ... very ready to pass into the metal. Thus with zinc there is obtained ... potential 1·57 volt, and even with copper there is a potential of ... volt (p. 645). If, however, the solution at the silver electrode ... . by a solution of potassium cyanide, then according to the .... of this the potential of silver sinks much below copper, ... with very concentrated solutions can even sink below zinc. In ... . of potassium cyanide the silver loses its character as ... . metal, and acquires that of a readily oxidisable one. This is ... . apparent chemically, for if silver powder is shaken with ... . of potassium cyanide it is fairly rapidly dissolved, and on

being acidified a white precipitate of silver cyanide is deposited from the liquid

Similar phenomena are often found in the case of substances which form complex compounds with silver (and other metals behave quite similarly). To find the explanation we shall first make ourselves acquainted with another, generally smaller, deviation from the potential series.

Cells can be constructed in which one of the metals, instead of being surrounded by a *solution* of its salt, is in contact with its *solid salt*. This is the case, for example, in the lead accumulator, one electrode of which is formed of lead in solid lead sulphate (p. 663). If the potential of such cells is investigated, it is found that the particular metal has always shifted its position in the potential series, and always, without exception, *towards the zinc end*. Thus in a cell of zinc and silver there is found, when the zinc electrode is left unchanged :—

Zinc against silver in silver nitrate .			1·57 volt
„	„	silver chloride .	1·06 „
„	„	silver bromide .	0·93 „
„	„	silver iodide . .	0·66 „

In the case of the iodide, therefore, the potential decreases by 0·91 volt, and is considerably different for the three "insoluble" salts.

The explanation is found on more closely studying the process which occurs on the passage of the current through such a cell. On the silver side the silver is transformed from the ionised state into the metallic. Argention, however, can exist only in *solution*. We must therefore conclude that, in spite of their apparent insolubility, all the above salts are really dissolved. This has also been proved in other ways for if as pure water as possible is shaken with silver chloride the electrical conductivity perceptibly increases, *i.e.* conducting ions pass into the liquid, and these can only be silver and chloride ions, since none other are possible.

Now, the work which is necessary for the separation of an ion from its solution depends not only on the nature of the ion, but also on its *concentration* in the solution, and it becomes all the greater the smaller the concentration. Conversely, a metal passes all the more readily into its ion the smaller the concentration of this in the solution in which it is to be formed. If this is correct the position of every metal must be shifted towards the zinc end, when it is placed in a solution which is less concentrated in respect of this ion, and *vice versa*. It must therefore be possible to construct cells which will exhibit an electromotive force, simply by placing the same metal in two solutions of one of its salts of different concentration. This is indeed the case, and the currents which are thereby produced act always in such a wise that the metal in the dilute solution is dissolved ; conversely, in the concentrated solution metal is deposited. In other words, the *currents tend to equalise the differences of concentration.*

state from solutions by means of reducing agents, it can assume a great
variety of colours according to circumstances.   It appears that the
yellow and brown forms of silver, more especially, which separate out
under the action of light on mixtures of silver salts and organic
substances (which have a reducing action), are amorphous; they are
more quickly attacked than the grey and black forms of silver and
also change into these under the influence of catalysers.

Metallic silver also has the property of passing into the *colloidal*
condition.   This colloidal silver is obtained by reducing silver in
alkaline liquids, and also when an electric arc is produced between
silver electrodes under water; by the latter means, the silver is first
volatilised and then suddenly precipitated in the surrounding water,
whereby it passes into the less stable form of colloidal silver.   These
solutions are of a brown or red colour; the forms of colloidal silver
obtained by chemical means dry up to masses with a metallic lustre,
the colour of which can be altered by slight influences, so that it passes
through all shades of yellow, red, violet, and green.   Notwithstanding
their metallic lustre, these masses do not behave like metallic silver,
since they do not conduct the electric current.   They are unstable
and are converted by many catalytic influences into ordinary white or
grey silver."

Silver is not attacked by dilute acids except *nitric acid*, which
readily dissolves it with evolution of nitric oxide and formation of
silver nitrate.   It dissolves to the sulphate, also, in concentrated boiling
sulphuric acid, whereby sulphur dioxide escapes.   It is very resistant
to basic substances; crucibles and dishes of silver are used in the labora-
tory in working with caustic potash and soda, as that metal is not
attacked to any considerable extent even on fusing these substances.

In the pure state silver is a white tenacious metal, which can be
readily drawn into wire, and made into very thin sheets by rolling or
hammering.   For use it is alloyed with 10 per cent of copper in order
to make it harder.   It conducts heat and electricity very well, and
occupies, in this respect, the first place among the metals.

The *combining weight* of silver is an important magnitude, since on
account of the excellent properties of its halogen compounds in
analysis, many other combining weights have been determined by
means of these.   The following method has been used in order to
establish the combining weight of silver with respect to oxygen.

Weighed quantities of silver chlorate were reduced to silver
chloride; since three combining weights of oxygen are contained in
one combining weight of chlorate, we have the proportion :

loss of weight of chlorate   3 × combining weight of oxygen
weight of silver chloride   combining weight of silver chloride

Thus, in one experiment, 103·980 gm. of silver chloride were

obtained from 138·789 gm. of silver chlorate. Since the threefold combining weight of oxygen is, in accordance with our assumption (p. 144), 48·000, the combining weight of silver chloride is 113·381.

Silver was now converted into silver chloride. If the combining weight of silver chloride is divided in the same ratio as that in which analysis has shown these elements to be combined in silver chloride, the two separate combining weights are obtained.

Thus, 144·207 gm. of silver chloride were obtained from 108·579 gm. of silver. We have therefore the proportion :—

$$Cl : Ag = (144·207 - 108·579) : 108·579,$$

where Cl denotes the combining weight of chlorine, and Ag that of silver. Hence :—

$$Ag = 107·93 \text{ and } Cl = 35·45.$$

677. **Argention.**—Silver forms only one kind of elementary ion, viz. monovalent argention, $Ag^{\cdot}$. Besides this, it can enter into many complex ions, especially such as contain nitrogen and sulphur.

Argention is colourless, and with respect to the properties of its compounds, it is allied to the monovalent ions of copper and mercury. On the other hand, there exist relations of isomorphism with sodium. It is the ion of a strong base, for the soluble silver salts react quite neutral, and exhibit no hydrolysis, although almost all the salts of the heavy metals do.

This is not in conflict with the fact that argention passes readily into the metal and is formed from this with difficulty, for we are dealing in the two cases with essentially different chemical relations and transformations. The heat of formation of argention from the metal has a large negative value; 106 k, must be absorbed in order that silver may pass into its ion. Metallic silver is also readily prepared from its salts; as a rule, contact with any organic substance, especially in light, is sufficient for this, these substances then becoming brown or black in colour owing to the finely divided silver which separates out.

Argention is a strong poison for all organisms. Its actions however are restricted by the chlorction, which is everywhere present, and with which it forms a difficultly soluble compound.

678 **Silver Oxide.** From the solutions of the silver salts soluble bases do not precipitate the hydroxide as one would expect, but its anhydride, *silver oxide*, Ag_2O. This is a brown powder which is sufficiently soluble in water to impart to it an alkaline reaction to vegetable dyes and which combines very readily with acids to form silver salts. In the laboratory it is used to remove halogen from dissolved halogen compounds, and to replace it by oxygen or hydroxyl. For this purpose it is freshly prepared, or after being

the two combining weights of the hydrogen of the thiosulphuric acid is replaced. Since it is assumed that one of these is present in the thiosulphuric acid as hydroxyl, the other as sulphhydryl, the further assumption is probable that the silver replaces the hydrogen of the sulphhydryl, because its power of combining with sulphur is certainly more highly developed than its power of combining with oxygen. The argentithiosulphanion which is here formed would therefore have the formula, $AgS \cdot SO_3$.

From the solutions obtained by the saturation of sodium thiosulphate with silver salts two different salts crystallise out. One of these is difficultly soluble, and its composition corresponds to the above formula, the hydrogen being replaced by sodium; the other is readily soluble, contains twice as much sodium, but its nature has not yet been cleared up. The formulae of these salts are $Na(SO_3 \cdot SAg)$ and $2Na(SO_3 SAg) + Na_2 S_2 O_3$.

The complex character of the compounds is proved not only by the solubility relations, but also by the fact that they both have a remarkably sweet taste, due to the ion $AgS \cdot SO_3'$, whereas otherwise the silver compounds have an unpleasant, metallic, astringent taste.

The formation of these compounds occurs when sodium thiosulphate is employed to dissolve difficultly soluble silver salts. This application is very widely extended in photography. If it is desired to separate the silver from them, an alkali sulphide, which precipitates silver sulphide from the solution, is the most suitable for the purpose. The solubility of silver sulphide is so small that it is practically completely precipitated even from the complex compound.

Sodium sulphite behaves similarly to sodium thiosulphate. A salt $Na(SO_3)Ag$, which is difficultly soluble in water, and which can be regarded as the sodium salt of argentisulphosion, is also known.

690. **Metallurgy of Silver.** Most of the silver is obtained as an admixture in lead in the preparation of the latter metal from ores (p. 665). For the purpose of separating the two metals use is made of the difference in their behaviour to oxygen. The lead containing silver is fused and exposed to the action of the atmospheric oxygen; the lead is thereby oxidised, its oxide flowing off as *litharge*, and the silver remains behind. The completion of the separation is recognised by the disappearance of the coating of lead oxide and the appearance of the lustrous surface of the silver (the *fulguration of silver*).

If the argentiferous lead, or *work lead*, is very poor in silver, it is more advantageous to separate it by means of a process of crystallisation into pure lead and an alloy richer in silver. This is done by allowing the fused work lead to slowly cool. *Pure* lead then crystallises out and a mother liquor, comparatively *rich in silver*, remains behind, just as from a salt solution pure water crystallises out as ice and a mother liquor richer in salt is formed. By continuing this separation, a condition is finally reached in which silver also begins to

If a small quantity of *B* is added to pure *A*, the melting point of the latter falls, in accordance with the general rule (p. 121), the depression being all the greater the larger the amount of *B* added. The change is almost proportional to the amount added, so that the corresponding temperatures are represented by an almost straight line *ak*.

The same considerations can be applied to *B*: from the point *b* a straight line must also sink towards the left representing the temperatures at which the liquid mixture is in equilibrium with solid B, i.e. the melting points of *B* in presence of the mixed liquid. The two lines will cut in a point *k*.

Now, along *ak* the liquid is in equilibrium with solid A, along *bk* with solid B. In the point *k*, therefore, the liquid is in equilibrium with both solid substances, and as the two lines cut only in one point, there is only *one* liquid mixture which is in equilibrium at one and the same time with the two solid substances.

This follows also from the phase law. We have two components, and in the point *k* four phases are present, viz. the liquid, the two solid substances, and vapour.[1] There is therefore no degree of freedom remaining, and all the variables, viz. pressure, temperature, and composition, have definite values.

If, therefore, any liquid mixture whatever is cooled, that one of the two substances will separate out which is in excess with respect to the composition represented by the point *k*. This continues with fall of temperature until the point *k* is reached. At this point the two substances separate out *at the same time* and in such proportions that the melting point and the composition of the liquid remain unchanged. A mixture corresponding to *k* behaves, therefore, like a *simple substance*, for it exhibits a constant melting point although it is a mixture. The relations are very similar to those in the case of acids of constant boiling point (p. 185).

Such a mixture of constant melting point is called a *eutectic mixture*, and the point *k* the *eutectic point*. The melting point of a eutectic mixture is, necessarily, always *under* that of its components, and is all the more so the nearer the melting points of the two pure substances are to one another. Fig. 122, in which various possible cases are represented, allows of these relations being readily seen.

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[1] If the vapour is excluded one degree of freedom is obtained, i.e. the point *k* alters every slightly with the pressure.

CHAPTER XXXVI

THALLIUM

692 General.—Thallium occupies a remarkable intermediate position between various other elements. By reason of the physical properties of the free element it is allied to lead, for, like this, it is soft, ductile, and has a high density. Its hydroxide, which is readily soluble in water, procures it a position along with the *alkali metals*, with which it is isomorphous in various compounds; its difficultly soluble halogen compounds bring it near to *silver*, *copper*, and *mercury*, and in another series of compounds it exhibits relations to the trivalent elements *aluminium* and *iron*.

Thallium was discovered by means of the spectroscope; all its compounds on being heated in the Bunsen flame, in which they quickly volatilise, give a green coloration which on being examined with the spectroscope appears as a single bright green line.

Thallium occurs only in small quantity in nature, but, like all the elements which can be detected in small amounts, it has been found to be fairly widely distributed. It is obtained as a by-product from the flue-dust in sulphuric acid works in which pyrites containing thallium is employed, and also, in association with zinc, from zinc ores. In the latter way it could be obtained in fairly large amounts if there were any demand for it.

As has already been mentioned, metallic thallium is very similar to lead, but is still softer. Its density is 11·9, its melting point 290°. It makes a grey mark on paper, but this soon disappears owing to oxidation. Fresh surfaces of the metal, which have an almost silver white appearance, quickly tarnish in the air through oxidation. In the potential series it stands between cadmium and iron, and is therefore a metal which readily replaces hydrogen from dilute acids. As a matter of fact, it dissolves in dilute acids which do not form difficultly soluble salts, *e.g.* sulphuric acid and nitric acid, and is precipitated in the metallic state from its solutions by zinc and cadmium.

Thallium forms two kinds of elementary ions, monovalent mono-thallion, Tl, and trivalent trithallion, Tl . The former conditions

the similarity of thallium to the alkali metals, the latter that to aluminium.

693. Thallous salts are formed with evolution of hydrogen by dissolving the metal in dilute acids. Solution in nitric acid, which takes place with reduction of the latter (very dilute acid yields hydrogen), also leads only to thallous nitrate. By means of free chlorine, however, thallous compounds can be converted into thallic compounds.

694. Monothallion is colourless; has, like lead, a poisonous action; and can be recognised by the formation of various difficultly soluble salts, especially the yellow iodide. It is not precipitated by alkali hydroxides and carbonates, and is thereby distinguished from the ions of all other heavy metals. Its heat of formation is almost zero, being only 7 kj.

695. Thallous Hydroxide, TlOH, is obtained by the decomposition of thallous sulphate with baryta, as a liquid with a strongly alkaline reaction which is dissociated into its ions, monothallion and hydroxidion, quite as extensively as the alkali hydroxides, and exhibits, therefore, the same basic properties. It turns red litmus paper blue, renders turmeric brown, and makes the skin of the fingers slippery when moistened with it. On evaporating the solution, the yellowish coloured hydroxide crystallising with H_2O is obtained; in contrast with the hydroxides of the alkali metals, this very readily loses the elements of water and passes into thallous oxide or Tl_2O, which is black-brown in colour. The dehydration takes place even at the temperature of the boiling water, so that on evaporating a solution of the hydroxide on the water-bath, black-brown lines are formed at the edges, but these immediately disappear when the acid is passed over them.

696. Thallous Sulphate, Tl_2SO_4, crystallises anhydrous in the rhombic forms of potassium sulphate, with which it is isomorphous. It is fairly soluble in water. With the sulphates of the trivalent metals, also, it forms double salts which crystallise in regular forms, and are perfectly analogous to the alums of the alkali metals. It can also form the corresponding monoclinic double salts with the divalent sulphates of the vitriol series.

697. Thallous Nitrate, $TlNO_3$, also crystallises anhydrous. It is soluble in about ten times its weight of water at room temperature, and melts at 205. By mixing it with other nitrates, masses can be obtained which melt at a comparatively low temperature; these find application as heavy liquids (solid thallous nitrate has the density 5·53).

698. Thallium Carbonate, Tl_2CO_3, is an anhydrous salt which dissolves in twenty times its weight of water, yielding a liquid with an alkaline reaction. The salt dissolves more readily in water containing excess of carbonic acid, but the acid carbonate is not known with certainty in the solid state.

The *phosphates* and *borates* of monothallion are also soluble in water, so that in this respect also thallium is allied to the alkali metals.

699. Thallous Sulphide. Tl$_2$S, is a brown-black precipitate which is formed by sulphuretted hydrogen in neutral, but not in acid solutions of thallous salts. The solubility and therefore also the conditions of precipitation are most nearly akin to those of zinc sulphide, although thallous sulphide appears to be somewhat more soluble. Accordingly, the precipitated sulphide redissolves in dilute acids.

700. Thallous Chloride.— In its halogen compounds thallium is most closely allied to silver, for these substances are white or yellow difficultly soluble powders which are sensitive to light: their solubility also diminishes with increasing combining weight of the halogen.

Thallous chloride, TlCl, is obtained as a white precipitate which slowly darkens in the light, when the ions of the salt come together in solution. About three hundred times its weight of water is required to dissolve it.

It is insoluble in ammonia, but dissolves in sodium thiosulphate with formation of a complex compound. It exhibits no tendency to form complex compounds with soluble chlorides; the salt is therefore precipitated from aqueous solutions on the addition of hydrochloric acid or chlorides, owing to the increase of chlor-ion. It is converted into soluble thallic chloride by treatment with chlorine under water.

701. Thallous Bromide is a yellow-white precipitate, the solubility of which is considerably less than that of the chloride, to which, however, in its other properties, it is similar.

702. Thallous Iodide is deposited as a yellow precipitate even from very dilute solutions, when its ions come together. It requires 12,000 parts of water for its solution, and, for known reasons, it is still less soluble in a solution of potassium iodide. This salt is employed for the detection and separation of thallium. In dilute acids it is not appreciably more soluble than in pure water, as it is the salt of the strong hydriodic acid (p. 499).

703. Thallous Fluoride is, in contrast with the other halogen compounds, a readily soluble salt.

The trivalent *trithallium* is of a somewhat yellowish colour, and is formed from monothallion only by fairly strong oxidising agents, such as chlorine or permanganate. Conversely, it very readily passes again into monothallion.

704. Thallic Hydroxide is obtained as a brown precipitate similar in appearance to ferric oxide, on adding soluble bases to a thallic salt. On being dried it assumes the composition TlO(OH), the freshly precipitated substance is probably Tl(OH)$_3$. On being heated, the hydroxide loses water and readily also oxygen, so that it passes into thallous oxide. Thallic oxide, Tl$_2$O$_3$, is also obtained when solutions of thallous salts are subjected to electrolysis; it separates on the

anode as a black coating, but it is difficult to obtain it of a definite composition.

Thallic hydroxide is a very weak base; its salts are greatly hydrolysed in aqueous solution, and when the dilution is fairly great almost all the hydroxide is precipitated from it, the acid remaining in solution. The most stable is the chloride, which can be obtained from the sub-chloride by means of chlorine. The bromide is less stable, and on attempting to prepare the iodide a mixture of thallous iodide and free iodine is obtained.

705. **Thallic Sulphate**, $Tl_2(SO_4)_3$, can form alums with the alkali sulphates. The double salt from thallous sulphate and thallic sulphate, which should also yield an alum, has, however, another form and a different amount of water of crystallisation; its composition is $Tl \cdot Tl(SO_4)_2 \cdot 6H_2O$, in which the one Tl is monovalent and the other trivalent.

The combining weight of thallium is $Tl = 204\cdot1$.

CHAPTER XXXVII

BISMUTH

General.—For the purposes of analysis, bismuth is classed along with the metals of the copper group, because it forms a sulphide which is insoluble in dilute acids as well as in alkali sulphides. According to its chemical affinity, however, it is so closely connected with antimony and arsenic, which belong to the last group, that it must be treated along with these, and is therefore suitably placed at the point of transition from the one group to the other. Of these elements it has the highest combining weight; for this reason, in accordance with the general rule, the basic properties are more strongly marked in it than in the case of its congeners. As the combining weight decreases, the latter rapidly lose their metallic character and the power of forming basic oxides, and finally lead to the non-metallic elements phosphorus and nitrogen, in which the acid forming properties are completely developed.

Metallic bismuth is a white, somewhat reddish metal of a well marked crystalline character; it is brittle, is not ductile, and falls to a powder when struck with a hammer. It melts as low as 270, and at a bright white heat passes into a vapour, the density of which leads to the molar weight 209, which coincides with the combining weight. It remains unchanged in the air, and is also very resistant to water. It is not attacked by dilute acids; its position in the potential series is between copper and silver, and it therefore inclines towards the noble metals. It therefore occurs in nature in many cases even in the *uncombined* state; it also occurs combined with sulphur as *bismuth glance*. Bismuth is readily dissolved by nitric acid with formation of bismuth nitrate and nitrous oxide.

Bismuth readily forms alloys with other metals whereby, in accordance with the general law, the melting point sinks. By the addition of lead, tin, and cadmium, alloys are obtained which liquefy even under 100, they fuse therefore in boiling water.

The combining weight of bismuth has been determined by weighing

the metal and the oxide obtained from it. It is not known with perfect certainty, and we shall take it as $Bi = 208.5$

707 Bismuthion.—Bismuth forms one kind of elementary ion, viz. the trivalent bismuthion, Bi'''. This is almost the only ion derived from bismuth, for the tendency of this metal to form complexes is extremely slight, and with the exception of some organic ions containing bismuth, others are scarcely known

Bismuthion is colourless and forms an extremely weak *base* with hydroxyl. As a consequence, the phenomenon of *hydrolysis* is so marked in the case of the bismuth salts that it can be regarded as a characteristic in analysis. Since the basic compounds which are hereby formed are difficultly soluble in water, the bismuth salts are *precipitated* by mere dilution with water; the precipitate is again dissolved on the addition of acids

The best known bismuth salt is the *nitrate*, which is obtained in hydrated crystals, $Bi(NO_3)_3 . 5H_2O$, by crystallisation from the solution of bismuth in nitric acid. On pouring water over these crystals, a snow-white, crystalline powder of a basic nitrate, $Bi(OH)_2NO_3$, is deposited, which is applied in medicine under the name of *bismuth subnitrate*. The nitric acid which is split off passes into the solution and enables another portion of the bismuth salt to remain dissolved. There exists, therefore, in the solution in respect of the precipitate of the basic salt, an equilibrium which is characterised by the fact that the concentration of the hydroxyl from the water is rendered sufficiently small by means of the hydrion of the free acid to allow the solubility product of the basic salt to be reached.

From solutions, bismuth hydroxide, $Bi(OH)_3$, is precipitated by excess of soluble bases. It is a white precipitate which is soluble neither in ammonia nor in caustic potash The former behaviour is due to the extremely slight development of its basic properties, the latter shows that it cannot, as many other weak bases do, split off hydrion and yield an anion containing oxygen

On being heated, the hydroxide loses water and is converted into bismuth oxide, Bi_2O_3, a yellow powder which, at a higher temperature, becomes reddish-brown, melts, and becomes crystalline on cooling

Bismuth sulphate, $Bi_2(SO_4)_3$, is obtained in the impure state by heating bismuth with concentrated sulphuric acid ; treatment with water converts it into the difficultly soluble basic sulphate $Bi_2(OH)_4SO_4$. With potassium sulphate it forms a well characterised double salt, $KBi(SO_4)_2$.

When *sodium thiosulphate* is added to bismuth salts, a clear liquid is formed from which, owing to decomposition, bismuth sulphide is slowly deposited. The solution probably contains the sodium salt of a bismuth thiosulphanion, for on the addition of potassium salts and alcohol a difficultly soluble precipitate of $K_3Bi(S_2O_3)_3 . H_2O$ is deposited, which is the potassium salt of the above ion. It has been

used to employ the precipitate, which is of a yellow colour, for detection and separation of potassium.

Bismuth Chloride, $BiCl_3$, is very readily formed from uth and free chlorine, the combination taking place with considerable evolution of heat. It is a white, soft, but crystalline substance becomes very dark in colour through excess of bismuth; this to the formation of a lower chlorine compound, perhaps $BiCl$, though no such substance has been prepared in the pure state. With the chloride at once deposits a snow white precipitate of basic ide, or rather, the anhydride of this, *bismuth oxychloride*, $BiOCl$ substance has a certain similarity to the monovalent chlorides of and mercury, not only as regards its external appearance and cult solubility, but also in its property of becoming grey in light. inence can be given graphically to this similarity by assuming in and in the similar compounds of bismuth, the monovalent ion which has been called *bismuthyl*. This is, however, so far, only mal assumption, since there is as yet no proof of the existence of an ion in the solution.

bismuth oxychloride, $BiOCl$, is so difficultly soluble in water that it is employed for the precipitation of bismuth. For that purpose only necessary to introduce chloridion in some form into the ion and then to dilute this. The dilation must be so much the er the more highly acid the liquid was at the commencement; it visable, therefore, when employing this method, to remove the s of acid by means of a base.

The *bromide* of bismuth is very similar to the chloride, and forms a very difficultly soluble *oxybromide* of a white colour.

Bismuth iodide is obtained from the elements or by the precipitation of bismuth salts with a large excess of potassium iodide, and is a red crystalline substance which is decomposed by water much slowly than the other halogen compounds. With much water an oxyiodide is formed as a fine red powder.

Bismuth iodide dissolves in hydriodic acid and forms hydrobisiodic acid, $HBiI_4 . 4H_2O$. With the iodides of the alkali metals alts of this acid are obtained; of these the potassium salt, $KBiI_4$, own in the form of ruby red laminae. The complex hydrobisiodidion, BiI_4', is, however, only slightly stable, and with much decomposes into bismuth oxyiodide and free hydriodic acid.

Bismuth Sulphide, Bi_2S_3, is obtained as a black brown ipitate on passing sulphuretted hydrogen into bismuth solutions. obtained crystalline by fusing metallic bismuth with sulphur, bismuth sulphide which is formed dissolves in the metal and, on ng, separates out in clusters. It occurs in nature as *bismuth* , and is used for the preparation of bismuth, which is obtained the glance by roasting and reduction of the oxide formed with oal.

Bismuth sulphide is insoluble in dilute acids, but dissolves with evolution of sulphuretted hydrogen on being heated with concentrated hydrochloric acid. It is not appreciably soluble in alkali sulphides, behaviour which is opposed to that of the sulphur compounds of its nearest congeners, antimony and arsenic. By fusing together bismuth sulphide and alkali sulphides, however, fine crystalline compounds, $KBiS_2$ and $NaBiS_2$, having a metallic lustre, can be obtained; these, however, rapidly oxidise in the air.

710. **Other Compounds**. It was mentioned above that a lower chloride of bismuth probably exists, although it is not known as a pure substance. The existence of a corresponding oxygen compound, BiO, has also been asserted. It is obtained as a dark brown powder by the careful treatment of bismuth hydroxide with reducing substances, or by heating basic bismuth oxalate.

A higher oxide of bismuth, *bismuth pentoxide*, Bi_2O_5, is obtained by heating the hydroxide with strong oxidising agents. Further, a mixture of bismuth oxide and caustic potash or soda when fused in the air is oxidised to a brown mass which, on being treated with water, deposits bismuth pentoxide contaminated with alkali. In the brown melt there possibly exists the alkali salt of a bismuthic acid; in aqueous solution, however, such salts cannot be obtained, as they are immediately hydrolysed. Bismuth pentoxide is obtained as a heavy, brown powder or as a hydrate of a red colour; it is insoluble in acids and bases, and is converted by hydrochloric acid into the trichloride, with evolution of chlorine.

711. **General**.—With antimony we commence the consideration of the metals of the tin group, in which a number of elements are classed together belonging to different natural families and forming corresponding sub-groups. Their common characteristic is the predominating tendency to form *acid* compounds in place of the basic ones yielded by the other metals. Their oxides, especially those comparatively rich in oxygen, behave as the anhydrides of acids, and their sulphur compounds dissolve in the solutions of the alkali sulphides with formation of *thio-salts* (*vide infra*). The last characteristic which is of importance in analytical chemistry has given rise to the formation of the whole group, and the relations which are here met with will be presently discussed in greater detail.

On account of the manifold and widely extending affinity relations existing between the elements, we shall repeatedly find resemblances to other groups, and it would be possible to class several of the elements considered here along with others previously discussed. By reason, however, of the variety of the relationships, a system of the elements, sufficient in all respects, cannot be framed, and the arrangement which has here been retained has therefore been determined chiefly by didactic considerations.

712 **Antimony**.—Antimony is allied on the one hand to *bismuth*, and on the other, to *arsenic* and *phosphorus*. It therefore forms a transition element between the metals and the non-metals, but is still essentially on the side of the metals. Its combining weight is $Sb = 120\cdot2$.

Antimony is a grey-white, lustrous metal, having the density $6\cdot7$; from the fused mass it solidifies in a distinctly crystalline form, and is at all temperatures so brittle that it can be easily ground or pounded to a powder. It melts at a red heat, and volatilises at a high temperature. The vapour exhibits a variable molar weight in the neighbourhood of 290. This number corresponds to no simple formula, but lies between Sb_2 and Sb_4; probably, therefore, we are dealing with a mixture of different kinds of vapour, perhaps Sb_4 and Sb_2.

In the potential series antimony stands beside bismuth; it does
not, therefore, decompose dilute acids, and it also remains unchanged
in the air. On being heated it readily oxidises; a piece of antimony
fused on charcoal before the blowpipe, continues to glow even after
the flame has been removed, the antimony burning to antimony oxide.
If a small globe of strongly heated antimony is thrown on a piece
of paper with upturned edges, it skips about on this, burning all
the while, and leaves very regularly marked, hyperbolic trails
(Fig. 123).

Besides the ordinary antimony, an *allotropic* form of less stability is

Fig. 123

known, which is obtained as a silver-white metal, of density 5·78, by
slowly decomposing a concentrated solution of antimony chloride in
hydrochloric acid with the electric current. The metal when so
deposited falls to a powder with slight explosion on being scratched
by a sharp body, ordinary grey antimony being formed with con-
siderable evolution of heat. This allotropic metal is not pure, but
contains antimony chloride, the amount of which varies with the
conditions of the experiment.

713 **Ions of Antimony**.—Antimony can form compounds of
the trivalent and of the pentavalent type; only the former of these,
however, yields a *basic hydroxide*, while the hydroxide of the higher
type is an *oxyacid*. They each show the basic and acid character

spectively only in a slight degree, and the number of well-characterised salts of antimony is therefore not large.

The compounds of the trivalent type are the better known and the more stable ; they are the only ones occurring in nature. The compounds of the pentavalent type are produced from the former by the action of strong oxidising agents, and can be readily reduced again.

The existence of a trivalent antimonion is probable, since there are solutions of antimony salts which behave in general like salts. These salts, derived from the base *antimony hydroxide*, $Sb(OH)_3$, are, however, greatly hydrolysed in water, and clear solutions can be obtained only with a large excess of acid. Consequently, the properties of the trivalent antimonion are not known with great exactness, and it can only be said with regard to it, that it is colourless and has a very poisonous action on the organism of the higher animals. In small quantities it acts as an *emetic*.

714. Antimony Hydroxide, $Sb(OH)_3$, is obtained as a white precipitate by the hydrolysis of the salts of antimony ; it readily loses water and is converted into the anhydride, antimony oxide Sb_2O_x. It can be converted into salts by treatment with concentrated acids ; these again undergo decomposition on dilution with water. It dissolves in caustic alkalis ; it has therefore the power of splitting off hydrion and of acting as an acid in a similar manner to alumina. The corresponding salts are reducing agents, and, for example, precipitate silver in the metallic state from its salts.

Antimony oxide, Sb_2O_3, crystallises readily and proves to be amorphous, crystallising either in regular or in rhombic form. The first form has the density 5·3, the second, 5·6. It has not yet been established which of the two forms is the more stable : it appears, however, to be the rhombic, since this occurs much more abundantly in nature. They are both, at all events, more stable than the hydroxide, since the latter, even under water, passes into the crystalline oxide.

715. Antimonious Chloride, or antimony trichloride, $SbCl_3$, is obtained from metallic antimony and chlorine by using excess of the former ; powdered antimony takes fire spontaneously on being allowed to fall into chlorine. It is obtained more cheaply by heating antimony sulphide with concentrated hydrochloric acid, whereby sulphuretted hydrogen escapes. The aqueous solution is evaporated and distilled, whereupon anhydrous antimony trichloride passes over. The remarkable fact that the chloride does not hereby decompose into hydrochloric acid and antimony oxide, as *e.g.* aluminium chloride does, although alumina is a stronger base, is probably due to the fact that in concentrated solution antimony trichloride is very slightly dissociated into its ions, and therefore undergoes hydrolysis in a correspondingly slight degree

Antimony trichloride is obtained as a white, crystalline, semi-solid

mass (*butter of antimony*), which melts readily and boils at 220°. It is
decomposed by water, difficultly soluble oxychlorides being deposited;
the composition of these depends on the amount of water, the amount
of chlorine which they contain being all the less the larger the quantity
of water

Of these, the compound $Sb_4O.Cl_2$, being a crystalline substance, is
best characterised, but even it decomposes into antimony oxide and
hydrochloric acid on being treated with more water.

Antimony trichloride combines with hydrochloric acid to form a
complex *hydroantimonichloric acid*, the salts of which are obtained by
allowing soluble chlorides and antimony trichloride to crystallise to-
gether.   The composition of these salts corresponds to various types,
and it has not yet been established whether we are dealing with vari-
ous complex acids or, partly, with double salts.   The most frequent
type is M_2SbCl_5, containing probably the trivalent anion $SbCl_6$.

716. **Antimony Tribromide**, $SbBr_3$, is formed with great rise
of temperature on bringing the elements together.   In its properties
it is very similar to the trichloride and, like it, decomposes with water
into basic bromide and free hydrobromic acid.   The boiling point is
270 , the melting point 95 .

717. **Antimony Tri-iodide**, SbI_3, is obtained from the elements
by warming, and crystallises in three different forms whose relative
degrees of stability have not yet been determined.   According to the
form, the colour of the crystals is dark red or green yellow; the
melting point of the form, stable at higher temperatures, is 167° the
boiling point, 400 ; the vapour of the tri-iodide is of a fine scarlet
colour.   With water it decomposes in the same manner as the other
halogen compounds ; the solution containing antimony, which is thereby
produced, is coloured yellow, from which the presence of undissociated
iodide in the aqueous solution can be concluded.   The precipitate of
oxyiodide is red to yellow in colour, and the colour is so much the
brighter the smaller the amount of iodine.

Antimony tri-iodide unites with the soluble iodides to form
complex salts, which belong chiefly to the type $MSbI_4$, with the anion
SbI_4'.

718. **Antimony Trifluoride**, SbF_3, is a white mass similar to
the trichloride, which can be dissolved in water without the separation
of precipitates.   This is probably due to very slight electrolytic dis-
sociation of the fluoride.   Complex salts are known with the alkali
fluorides.

719. **Antimony Trisulphide.**—The compound Sb_2S_3 occurs in
nature as the most widespread ore of antimony, and is called *antimony
glance* (or stibnite).   It is a grey substance crystallising in long needles
of a metallic lustre ; it readily melts, and on being heated in the air,
passes into antimony oxide, the sulphur being burned.

From solutions of trivalent antimony, the trisulphide is pre-

proposed to employ the precipitate, which is of a yellow colour, for the detection and separation of potassium.

708. **Bismuth Chloride**, $BiCl_3$, is very readily formed from bismuth and free chlorine, the combination taking place with considerable evolution of heat. It is a white, soft, but crystalline substance which becomes very dark in colour through excess of bismuth; this points to the formation of a lower chlorine compound, perhaps $BiCl$, although no such substance has been prepared in the pure state. With water, the chloride at once deposits a snow-white precipitate of basic chloride, or rather, the anhydride of this, *bismuth oxychloride*, $BiOCl$ This substance has a certain similarity to the monovalent chlorides of silver and mercury, not only as regards its external appearance and its difficult solubility, but also in its property of becoming grey in light. Prominence can be given graphically to this similarity by assuming in this and in the similar compounds of bismuth, the monovalent ion BiO, which has been called *bismuthyl* This is, however, so far, only a formal assumption, since there is as yet no proof of the existence of such an ion in the solution.

Bismuth oxychloride, $BiOCl$, is so difficultly soluble in water that it can be employed for the precipitation of bismuth. For that purpose it is only necessary to introduce chloridion in some form into the solution and then to dilute this. The dilution must be so much the greater the more highly acid the liquid was at the commencement; it is advisable, therefore, when employing this method, to remove the excess of acid by means of a base.

The *bromide* of bismuth is very similar to the chloride, and forms also a very difficultly soluble *oxybromide* of a white colour.

Bismuth iodide is obtained from the elements or by the precipitation of bismuth salts with a large excess of potassium iodide, and is a black-red crystalline substance which is decomposed by water much more slowly than the other halogen compounds. With much water bismuth oxyiodide is formed as a fine red powder.

Bismuth iodide dissolves in hydriodic acid and forms hydrobismuthiodic acid, $HBiI_4 . 4H_2O$. With the iodides of the alkali metals the salts of this acid are obtained; of these the potassium salt, $KBiI_4$, is known in the form of ruby-red laminae. The complex hydrobismuthiodidion, BiI_4', is, however, only slightly stable, and with much water decomposes into bismuth oxyiodide and free hydriodic acid.

709. **Bismuth Sulphide**, Bi_2S_3, is obtained as a black-brown precipitate on passing sulphuretted hydrogen into bismuth solutions. It is obtained crystalline by fusing metallic bismuth with sulphur; the bismuth sulphide which is formed dissolves in the metal and, on cooling, separates out in clusters. It occurs in nature as *bismuth glance*, and is used for the preparation of bismuth, which is obtained from the glance by roasting and reduction of the oxide form charcoal.

The naturally occurring antimony glance is employed for the preparation of metallic antimony. The red, amorphous form is used as a dye under the name antimony vermilion; red, vulcanised indiarubber is coloured with antimony sulphide

720. Complex Antimony Compounds.—Trivalent antimony has, in a very marked degree, the property, already mentioned in the case of other hydroxides, of forming complex compounds with organic substances containing several hydroxyl groups. The most important of these is the compound with *tartaric acid*, which yields an *antimonial tartaric acid*; in contrast with the ordinary antimony compounds this compound is not dissociated hydrolytically by water, so that it can be dissolved, and the solution diluted without the separation of basic substances. The exact discussion of these compounds must be reserved for organic chemistry; they have been mentioned here because tartaric acid is employed in analytical chemistry for the purpose of preparing clear, dilute solutions of antimony salts. For this purpose the addition of a solution of tartaric acid to the liquid is sufficient. The formation of the complex compound takes place so quickly that the desired result is attained in a few moments. From such solutions antimony sulphide is precipitated by sulphuretted hydrogen, showing that the complex yields sufficient antimonion for the solubility product of antimony trisulphide to be exceeded.

721. Antimony Pentachloride. By means of oxidising agents it is possible to pass from compounds of trivalent to those of pentavalent antimony. If chlorine is passed over antimony trichloride, a heavy liquid which fumes in the air is produced; this is also obtained from antimony and chlorine by using excess of the latter At 140° it commences to boil, and the determination of the vapour density shows that it exists in the vaporous condition for the greater part undecomposed. Chlorine is, however, very readily split off, and even when the boiling is continued, so much of it escapes that there remains a considerable residue of trichloride. On the whole, therefore the compound behaves similarly to phosphorus pentachloride (p. 560), but is somewhat more stable.

Antimony pentachloride unites with water and forms various hydrates which, however, are formed only when a small quantity of water is used, clear solutions being then produced; when dissolved in much water, it undergoes complete hydrolysis, and difficultly soluble antimonic acid is deposited. It combines with hydrochloric acid to form a fairly stable, crystalline substance, which dissolves without decomposition in a small quantity of water, and has the composition $H_6SbCl_{10} \cdot 10H_2O$.

An antimony pentabromide is not known; the existence of the pentaiodide is also doubtful.

722. Antimonic Acid. Antimonic acid, $Sb(OH)_5$, or its anhydrides, is obtained by the decomposition of antimony pentachloride

ipitated by sulphuretted hydrogen as a yellow-red, non-crystalline
substance which, on being gently heated, passes into grey, crystalline
antimony sulphide. Conversely, when fused stibnite is quickly cooled,
an amorphous mass is obtained which is translucent, and of a dark-red
colour, and becomes yellow-red on being powdered. The relation
which here exists is therefore similar to that between amorphous and
crystalline sulphur, the amorphous form being the less stable: the
velocity of transformation, however, at the ordinary temperature is so
small that it cannot be observed.

Antimony sulphide is not appreciably soluble in dilute acids; it
dissolves in strong hydrochloric acid with evolution of sulphuretted
hydrogen. For this reason antimony is precipitated by sulphuretted
hydrogen from acid solution, provided that the solution is dilute with
respect to the acid. When antimony sulphide has been brought into
solution with concentrated hydrochloric acid, and if the liquid which
contains sulphuretted hydrogen is diluted, a precipitate of yellow-red
antimony sulphide is obtained. The remarkable phenomenon that a
precipitate (not due to hydrolysis) is produced by dilution with water,
is explained by the fact that the antimony trichloride present in con-
centrated solution contains the antimony almost entirely in the form
of an undissociated compound (p. 709), the antimonion necessary
for the reaction with the sulphuretted hydrogen is formed only on
dilution.

Antimony sulphide readily dissolves in the *alkali sulphides*, especially
the polysulphides. A compound of the pentavalent series is thereby
formed, when excess of sulphur is present, and the reaction will be
discussed later in greater detail.

Antimony sulphide also dissolves in concentrated and hot solutions
of the alkali hydroxides and carbonates; on cooling and diluting, it is
again precipitated as a brown powder. This precipitate was formerly
applied in medicine under the name *kermes*; since, however, it is a
variable mixture of amorphous antimony sulphide and antimony
oxide, its medicinal action varies according to the method of its pre-
paration. The reaction which here occurs has not yet been sufficiently
explained; we are dealing essentially with the formation of the alkali
salts of antimony oxide (p. 709), and of the corresponding compounds
of antimony sulphide, which are stable in hot, concentrated solution,
whereas on cooling and on dilution, the equilibrium is again shifted in
the opposite sense, *i.e.* antimony sulphide is again formed.

Use is made of the precipitation of the antimony compounds
by sulphuretted hydrogen for the detection and estimation of
antimony. Since the amorphous precipitate, even after being dried
at 100°, still contains appreciable quantities of water, it is, in quanti-
tative estimations, converted by careful heating in an atmosphere
free from oxygen (in a current of carbon dioxide), into the grey,
crystalline form which is of constant composition.

acid, but contains sulphur in place of oxygen.   We have already
(p. 418) met with such a compound in the case of thiocarbonic ac.
and the relationships which are found were explained there.

In the case of the metals grouped together in the present class
the formations of such thio ions is a general phenomenon, and th
solubility of their sulphides in alkali sulphides is due to the formation
of soluble alkali salts of such thio ions.

As in the case of the oxyacids, the higher compounds, i.e. those
richer in sulphur, have the more strongly acid character.   For this
reason, antimony trisulphide is only very slightly soluble in the dilute
solutions of the alkali *mono*sulphides, but is readily soluble in the
yellow solutions which contain *poly*sulphides.   In the former case a
salt of thioantimonosion, SbS_3''', would be formed ; such an ion, how
ever, does not exist, and the saline compounds corresponding to it
which are formed to a certain extent in concentrated solutions, are
decomposed by water.   The salts of thioantimonic acid, however, are
very stable, and these are immediately formed when the necessary
sulphur can be obtained from the polysulphide present.

Free thioantimonic acid, H_3SbS_4, is not known.   If hydrion is
introduced into the solution of one of its salts, sulphuretted hydrogen
and antimony pentasulphide are formed $2H_3SbS_4 = Sb_2S_5 + 3H_2S$.
The process corresponds exactly to the formation of an anhydride with
separation of water, the place of water being taken by sulphuretted
hydrogen in the case of the thio-acid.

The *antimony pentasulphide* which can be obtained in this way is
very similar to the amorphous trisulphide as far as external appearance
is concerned.   It readily decomposes into trisulphide and sulphur, so
that amounts of sulphur varying with the previous treatment can be
extracted from the product with carbon disulphide.   It is soluble not
only in the monosulphides of the alkali metals, but also in the
hydroxides ; in the latter case, antimonate is formed in the solution
along with thioantimonate, or, the salts of an antimonic acid in which
only a part of the oxygen is replaced by sulphur are formed   It
dissolves even in the alkali carbonates, although with somewhat
greater difficulty.   The pentasulphide obtained by precipitation from
Schlippe's salt is employed in medicine under the name "*gold*
sulphur of antimony."

The solutions of the thioantimonates mostly give precipitates with
the salts of the heavy metals which are practically insoluble in water
and are coloured yellow, red, or black.   These compounds are like
Schlippe's salt—salt-like compounds of trivalent thioantimonanion.

724.   **Antimony Hydride**.—The relationship of antimony to
nitrogen and phosphorus is seen with especial clearness in its power
of forming a gaseous compound with hydrogen, SbH_3, which, as
regards its composition, belongs to the same type as ammonia and
phosphoretted hydrogen.   This compound, certainly, has no basic

properties, but this constitutes no essential difference, since these are practically wanting even in the case of phosphoretted hydrogen.

Antimony hydride, SbH$_3$, is obtained by the action of acids on alloys of antimony with other metals which decompose acids, especially zinc. In this way the antimony hydride is always obtained mixed with much hydrogen. It can be separated from the mixture by strongly cooling, but on volatilising the separated mass, it very readily decomposes and can be preserved for some hours only by employing special precautions. Its smell recalls that of hydrogen sulphide.

If the mixture is passed through a glass tube heated at one part, the antimony hydride decomposes at that spot, and metallic antimony is deposited as a grey-black coating, which, on being heated, runs together into drops, but cannot be readily volatilised. It differs in this respect from the "arsenic mirror," which is formed under similar conditions, and with which it could be confused. Further differences will be given under arsenic.

Antimony hydride burns with a white flame; if a piece of porcelain is held in this, unburnt antimony is deposited on it as a black soot, which is converted at the edges into white, floury-looking antimony oxide. The antimony stains can be readily distinguished from the arsenic stains formed under similar conditions, by their grey (not brown) colour.

In a solution of silver nitrate antimony hydride produces a black precipitate which contains silver and all the antimony, so that the solution contains only nitric acid and undecomposed silver nitrate.

725. Alloys of Antimony.—Of the various metallic mixtures for which antimony is employed, the most important is that with *lead*. Even fairly small quantities of antimony considerably increase the hardness of lead, and in chemical manufactures, where the chemical resistibility of lead is required along with moderately great mechanical resistibility, such alloys, called *hard lead*, are employed. *Type-metal*, also, which, along with a comparatively easy fusibility, must possess a sufficient hardness and the power of exactly filling out the mould, consists essentially of lead and antimony. Alloyed with tin, antimony yields *Britannia metal*, which is used for domestic utensils.

CHAPTER XXXIX

ARSENIC

726. General. In accordance with its smaller combining weight, arsenic deviates still more than antimony from the type of the metals, and exhibits greater similarity to the non-metal phosphorus; at the same time the tendency to form acid compounds increases. In fact, the resemblance of arsenic to phosphorus is so great that it might also have been treated along with that element among the non-metals.

Elementary arsenic occurs in various forms, which partly recall those of phosphorus. The most stable form is a grey, crystalline mass with a metallic lustre. On being heated arsenic does not fuse, but passes, before reaching its melting point, into a brown-yellow vapour. It can be fused by heating under pressure; it then solidifies to a steel-grey, lustrous mass with a crystalline fracture.

From the vapour density of arsenic the molar weight is found to be 300, since the combining weight may be taken as 75, arsenic vapour has the formula As_4. In this respect, also, there is a similarity to phosphorus (p. 357) and a dissimilarity to the metals, in the case of which the molar weight coincides with the combining weight.

If the vapour of arsenic is quickly cooled *amorphous arsenic* is produced, various kinds of which are known. The most interesting of these is obtained by very rapid and powerful cooling; it is yellow, non-metallic, and is soluble in carbon disulphide; it rapidly undergoes oxidation in the air with faint luminescence, and emits a smell of garlic; in short, it is very similar to white phosphorus. To a certain extent it differs from it in the great velocity of its spontaneous transformation into the more stable form, which is greatly accelerated by light.

At the same time, other kinds of amorphous arsenic are formed, more especially a velvet black and a grey variety. All these forms are unstable, and are rapidly converted, especially when warmed, into stable, crystalline arsenic. Their formation affords fresh examples of the principle that the unstable forms are produced before the stable.

That as a rule, only the crystalline form appears to be formed

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the vapour, is due to the fact that the phosphorus-like arsenic produced changes almost instantaneously into the more stable ... Only when the velocity of this change is diminished to a ... value by rapid cooling at a low temperature can the unstable ... first produced be observed.

87 Arsenic Trioxide.—When arsenic is heated with access of ... it burns with a brilliant white flame, forming an oxygen com... to which, in accordance with its composition and vapour density, ... formula As_4O_6 must be assigned. For it contains 24 parts of ... to 75 parts of arsenic, and its vapour density yields the molar ... 396 Strictly speaking, therefore, this compound would have ... called arsenic hexoxide, but one has become accustomed to write ... formula As_2O_3 and to call the substance arsenic trioxide. In ... life, in which this compound plays a certain rôle, it is called ... *arsenic* or simply *arsenic*.

... arsenic trioxide occurs in various forms. When manufactured on ... large scale it appears in the first instance as a transparent glass, ... is generally coloured slightly yellow by traces of impurities. ... glass is *amorphous* arsenic trioxide. On being kept some time ... glass becomes milk-white and looks like porcelain: since this ... is accelerated by the moisture in the air, it proceeds from the ... towards the interior. On breaking a moderately large piece, ... therefore, which has on all sides assumed a porcelain-like appearance, ... of unchanged glassy substance is frequently found in the ... The porcelain-like mass is *crystalline* arsenic trioxide. Since ... produced spontaneously from the amorphous form, it is the ... stable of the two, and in accordance with a general law (p. 261) ... in all solvents less soluble than the amorphous form When, ... therefore, water is in contact with the two forms the solution which ... saturated in respect of the amorphous form will be supersaturated ... respect of the crystalline form. The amount of the latter will ... therefore increase from the solution; this becomes unsaturated in ... of the amorphous form, dissolves fresh quantities of it, and ... deposits it as crystals. This process is continued until all the ... amorphous substance is converted into crystalline. This furnishes ... explanation of the accelerating influence of moisture on the ... formation (cf. p. 676).

... Larger crystals of arsenic trioxide are obtained by dissolving the ... substance in warm hydrochloric acid. On cooling, it separates out ... slowly and forms regular octahedra with a diamond-like lustre. ... formed crystals can also be obtained by sublimation. Arsenic ... oxide, like metallic arsenic, also passes without fusion into vapour. ... Besides the regular form of arsenic trioxide, a monoclinic, pseudo- ... form also exists. It occurs (rarely) in nature, and as a mineral ... called *claudetite*. The stability relations of the two crystalline ... have not yet been determined.

In the manufactures, arsenic trioxide is obtained by roasting arsenical ores. The trioxide is collected by leading the vapours produced through chambers and passages of masonry, in which the trioxide is deposited as a powder known as "*poison flour*." This is purified by resublimation from iron pots having cylinders placed over them, and is thereby obtained in the glassy form.

Arsenic trioxide is only sparingly soluble in water. On placing the powder in water it is not wetted, and owing to the surface tension, it remains floating on the water although its density is 3·7. The heat of formation of the trioxide As_2O_3 is 647 *kj*.

Arsenic trioxide readily loses oxygen. In order to show this, a small glass tube is drawn out to a point, and fused off: a particle of arsenic trioxide is then placed in the point, and above it a small piece of freshly ignited wood charcoal. If the tube is so heated that the charcoal is first caused to glow and then the arsenic trioxide volatilised, the latter loses its oxygen in contact with the charcoal, and the liberated arsenic is deposited as a black coating on the colder portions of the tube. This "*arsenic mirror*" can be easily recognised by its feebly metallic lustre and the brown colour which it shows in thin layers by transmitted light. By means of this experiment very small quantities of the trioxide can be detected with certainty.

When greatly diluted, arsenic trioxide is used as a medicament. It is remarkable, also, that the organism of man and the animals can gradually become accustomed to large quantities of arsenic. By means of it horses acquire a healthy and spirited appearance, and arsenic eaters also assert that they can undergo much more bodily exertion under the influence of this substance. The organism accustomed to arsenic, however, rapidly decays when the use of this substance is interrupted, and it can be kept in an active condition only by regular or increased doses of the poison.

728. **Arsenious Acid.**—The aqueous solution of arsenic trioxide has a feebly acid reaction, and contains an acid which is formed from the trioxide by the addition of the elements of water. A decomposition takes place in the process, so that the acid contains only one combining weight of arsenic. Which of the two hydrates H_3AsO_3 and $HAsO_2$ *predominates* in the solution (for we must assume that both are present, although in very varying amount) is unknown; at all events, the acid present in the solution behaves as a feeble monobasic acid, and the formula $HAsO_2$, with the ions $H^{\cdot}$ and $AsO_2^{\prime}$, will therefore be the most appropriate representation of the facts.

The electrolytic dissociation of arsenious acid is extremely small; its soluble salts are therefore dissociated hydrolytically to an appreciable extent, and the alkali salts, more especially, have an alkaline reaction. The salts of the other metals correspond to the orthoacid H_3AsO_3, and are mostly very slightly soluble in water. This is true more especially for the ferric salt, so that freshly precipitated ferric

hydroxide by combining with the arsenious acid can be used as an effective antidote in cases of poisoning with this substance. The copper salt is green, and is employed as a colouring matter (*Schule's green*). With copper acetate, copper arsenite forms a double salt of a brilliant green colour, which is applied under the name *Schweinfurter green*. On account of their containing arsenic, both substances are dangerous, and their use for articles of daily use, and more especially also in wall papers, must by all means be excluded.

729. Arsenic Trichloride.—In a current of chlorine, arsenic burns without external application of heat and forms a colourless, heavy liquid (density 2·2), which boils at 134°, and whose vapour yields the molar weight 182. The latter number forms the chief reason for assigning to arsenic the combining weight 75, and to its chloride the formula AsCl₃, for 75 is the smallest weight of arsenic occurring in a mole of any volatile arsenic compound.

Arsenic trichloride can also be obtained by pouring sulphuric acid over arsenic trioxide and adding pieces of rock salt. By the action of the sulphuric acid on the sodium chloride, hydrochloric acid is formed, and this acts on the arsenic trioxide according to the equation $As_2O_3 + 12HCl = 4AsCl_3 + 6H_2O$. Since, on the other hand, arsenic trichloride is partially converted by water into trioxide and hydrochloric acid, the method is successful only when a large excess of concentrated sulphuric acid is employed whereby the water produced is bound.

A chemical equilibrium, which depends on the concentration of the four substances, exists between water, arsenic trichloride, hydrogen chloride, and arsenic trioxide. An increase of the water promotes the decomposition of the trichloride; an increase of hydrogen chloride, its re-formation. That ordinary aqueous hydrochloric acid also converts part of the trioxide into chloride, is seen from the increased solubility of the trioxide in concentrated hydrochloric acid as compared with that in water; the excess is dissolved as chloride.

The presence of the chloride in the hydrochloric acid solution is also made evident from the fact that on distillation an arsenical distillate is obtained. Since arsenic trioxide or arsenious acid is not volatile under these conditions, the arsenic can pass into the distillate only in the form of volatile trichloride. This behaviour is of importance for the treatment of arsenical substances in analysis. Solutions containing arsenious acid and hydrochloric acid cannot be evaporated without a danger of loss of arsenic.

In order to avoid this we may either make the liquid alkaline before evaporating it, or the arsenious acid may be converted by an oxidising agent into arsenic acid. A solution of the latter can be evaporated without loss even when strongly acidified with hydrochloric acid. For arsenic does not form any pentachloride corresponding to arsenic acid, nor any other volatile chlorine compound belonging to this stage of oxidation.

* The above gives a means of purifying sulphuric acid containing arsenic. The arsenic is reduced to arsenious acid (if it is not already in this condition), and hydrogen chloride is passed through the heated acid ; the arsenic is then volatilised as the trichloride.

* Conversely, hydrochloric acid can be freed from arsenic by oxidising the latter to arsenic acid and distilling the acid. The arsenic remains in the residues.

Arsenic forms similar compounds with bromine and iodine, $AsBr_3$ and AsI_3 ; these have a higher boiling point and melting point. At room temperature they are both solid ; the bromide melts at ?? and boils at 220 ; the melting point and boiling point of the iodide are not definitely known, but they are both higher than in the case of the bromide.

The compounds are obtained by bringing together the free elements ; this is best done under carbon disulphide, which can then be removed by evaporation. The bromide is colourless, the iodide red. Like the *chloride*, both compounds are decomposed by water ; the relative amount of the portion dissolving without decomposition is not known. The heats of formation are : $AsCl_3$ 229 k, $AsBr_3$ 188 k, AsI_3 53 k.

730. Arsenic Trisulphide.—Arsenic trisulphide, As_2S_3, corresponding to the trioxide, occurs in nature. It forms yellow crystals with a slight metallic lustre ; on being ground it yields a bright lustrous powder, which was formerly used as a pigment. To this the name *orpiment*, the mineralogical name for arsenic trisulphide, is due. In older writings it is also often called *sandarac*. Arsenic trisulphide is obtained as a sulphur-yellow powder, practically insoluble in water, by precipitating acid solutions of arsenious acid with sulphuretted hydrogen. Since this is the way in which arsenic is ordinarily separated in analytical operations, it is important to know the exact properties of arsenic trisulphide.

On treating a dilute solution of arsenious acid in pure water with sulphuretted hydrogen, the smell of the gas disappears ; no precipitate is formed, but the solution becomes yellow. If a cone of convergent light rays is allowed to fall on the liquid, the path of the light becomes bright, owing to diffusion. This fact (and the polarised condition of the diffused light) shows that the arsenic trisulphide in the liquid is not really in solution, but is in suspension in a state of very fine division. The particles are, however, so small that they are neither visible under the microscope nor are retained by filter paper. Their size is of the order of a wave-length of light.

If some hydrochloric acid is added to the liquid it becomes turbid, and in a few moments arsenic trisulphide separates out in yellow flakes. Other substances, acids and neutral salts, act in the same manner as hydrochloric acid, and in a way that is fairly independent of their chemical nature. Great differences are, however, found

according to the valency; precipitation is caused by a small concentration of divalent and by a still smaller concentration of trivalent cations. If the precipitate is placed as quickly as possible after its separation on a filter and the acid washed away with pure water, it again partly passes into a liquid as before; another portion remains insoluble. If the precipitate is allowed to remain some time in the solution in which it was formed, it becomes completely insoluble. We again recognise here the properties of *colloidal solutions* (p. 427). The formation of such colloidal solutions takes place most easily in pure water. Addition of foreign substances, especially of a saline character to which free acids and bases also belong, causes the separation of the colloidal substances in the form of amorphous flakes. For this reason the colloidal solution of arsenic trisulphide can be obtained with sulphuretted hydrogen only from a pure solution of arsenious acid. If the solution contain, for example, hydrochloric acid along with the arsenious acid, the arsenic trisulphide is at once formed as a flocculent precipitate on being treated with sulphuretted hydrogen.

If the yellow colloidal solution is kept some time it becomes more and more turbid, and gradually deposits more and more of the arsenic trisulphide as a precipitate. This is also a general property of colloidal solutions; the dissolved substance passes in time spontaneously into an insoluble form.

The characteristic difference between colloidal solutions and the true solutions, viz. that the former do not exhibit any elevation of the boiling point nor depression of the freezing point as compared with pure water (p. 427), is also found in the case of colloidal arsenic trisulphide.

Arsenic trisulphide, not in the colloidal condition, is practically insoluble in water and acids; more especially, it is not attacked by fairly concentrated hydrochloric acid, and thereby differs essentially from antimony trisulphide. It is readily oxidised by nitric acid to arsenic acid and sulphuric acid. On standing in a moist condition in contact with the oxygen of the air, it is also readily oxidised.

Arsenic trisulphide is readily soluble in alkaline liquids of all kinds, caustic alkalis, alkali carbonates, ammonia, and also ammonium carbonate; it also dissolves in soluble sulphides and hydrosulphides. Various salts are contained in the solutions according to the solvents used; these may be regarded as arsenites in which some or all of the combining weights of oxygen are replaced by sulphur. We are therefore dealing with the salts of thioarsenosion, and the members intermediate between these and the salts of arsenious acid. In the latter case we are dealing with mixtures the nature of which has not yet been explained. Arsenic trisulphide is again precipitated from all these solutions by the addition of acids.

By means of its solubility in ammonium carbonate arsenic

3 A

120°. It fumes strongly in the air as it undergoes decomposition with water; it dissolves in water with considerable evolution of heat, forming a clear liquid. This still contains, especially when concentrated, a portion of the chloride dissolved unchanged, for on heating this passes over with the steam. The greatest part is, however, hydrolytically dissociated, and the dilute solution contains essentially hydrochloric acid along with colloidally dissolved stannic hydroxide. This is proved by the fact that the solution exhibits all the properties of a correspondingly dilute solution of hydrochloric acid, and also by the fact that in course of time the greater portion of the tin separates out as a white, gelatinous precipitate of stannic hydroxide.

When small quantities of water are allowed to combine with stannic chloride, rise of temperature being avoided, various hydrates are formed with from three to nine moles of water of crystallisation, the first of which is the most stable. They are crystalline substances which dissolve in water, and yield solutions which exhibit the same properties as the solution of the tetrachloride when prepared directly.

The tetrachloride combines with hydrochloric acid to form a hydrostannichloric acid, H_2SnCl_6, which can also be obtained in the solid state with $6H_2O$. The crystals melt as low as 28°. The acid forms good crystalline alkali salts, which are also formed from the tetrachloride and the respective alkali chlorides. The ammonium salt, $(NH_4)_2SnCl_6$, crystallises anhydrous, and is used as a mordant in dyeing under the name of *pink salt*.

Stannic hydroxide, which slowly separates out from the aqueous solution of stannic chloride, is immediately obtained by saturating the solution with a base. A gelatinous precipitate of $Sn(OH)_4$ is formed, which dissolves in dilute acids; from these solutions it again separates spontaneously after some time. We are probably dealing here with a colloidal solution which undergoes decomposition, for the reason that the stannic hydroxide is slowly converted into another less soluble form. The same transformation also occurs in the original hydrochloric acid solution, for the hydroxide precipitated from solutions of different ages has different properties.

The precipitate redissolves in excess of caustic potash or soda, a stannic salt or *stannate* being formed. The solution has a strongly alkaline reaction, showing that the salt is hydrolytically dissociated. From the solution in caustic potash a salt, K_2SnO_3, can be obtained in crystals; in this case, therefore, the stannic acid forms a divalent stannanion SnO_3, which is comparable with carbanion CO_3. A number of other salts are also known containing several combining weights of tin to two of potassium, and are therefore salts of "condensed" stannic acid; they are, however, as a rule not well characterised, and are unstable.

Differing from this stannic acid there is another compound of the

The fume of the arsenical hydrogen is white, and deposits on cold
[...] held in it a brown-black film of metallic arsenic. A black
[...]late is produced in a silver solution.

All these reactions are very similar to those of antimony hydride
[...] and it is therefore of importance to distinguish between
[...] For this purpose a solution of sodium hypochlorite may be
[...] amply used.   In this the arsenic mirror speedily dissolves, while
[...] mony mirror remains for a long time unchanged.   Further,
arsenic mirror is readily volatile, the antimony mirror is not.
[...]rified hydrogen or ammonium sulphide vapour converts the
[...] into bright yellow arsenic sulphide, insoluble in hydrochloric
[...] the latter into yellow-red antimony sulphide, soluble in hydro-
[...] acid. The precipitate produced in silver solutions by arsenic
[...] is silver, the arsenic passing into solution as arsenious acid.
[...]mony hydride forms silver antimonide, and there is no antimony
[...]lution.   The last reaction affords a means of analysing mixtures
[...] two hydrogen compounds.

732. Compounds of Pentavalent Arsenic.—The compounds
[...]erto discussed can all be referred to the trivalent type. Besides
[...]atter, arsenic forms two other series of compounds, one of which
[...]sponds to the pentavalent type, while there are also other com-
[...]ds which point to the existence of a divalent type. The latter
[...]comparatively rare and unimportant.

When arsenic trioxide is treated with oxidising agents, e.g. nitric
[...] a solution is obtained from which, on greatly concentrating,
[...] acid, H_3AsO_4, crystallises out.

In its whole behaviour arsenic acid is very similar to orthophos-
[...]ic acid.   Like this it is tribasic, but its soluble, normal salts are
[...]tially hydrolysed on being dissolved in water, and therefore react
[...]line.   All the salts of arsenic acid are isomorphous with the corre-
[...]ding salts of phosphoric acid ; in fact, it was in the case of the
[...]nates and phosphates that similarity of form along with corre-
[...]ding composition was first observed.

The solubility relations of the salts of arsenic acid have also a very
[...] similarity to those of the salts of the phosphoric acids.

The following differences, however, exist in the behaviour of
[...] two substances.   In the first place, one has not succeeded in
[...]paring partial anhydrides of arsenic acid, corresponding to pyro-
[...]osphoric and metaphosphoric acids.   On the contrary, only ortho-
[...]nic acid, H_3AsO_4, along with its salts, and arsenic pentoxide are
[...]own.

Further, even on being gently warmed, arsenic acid loses water
[...] passes into its anhydride, *arsenic pentoxide*, As_2O_5 ; while phos-
[...] acid (p. 369) can be dehydrated, by heating, only to meta-
phoric acid.

Arsenic pentoxide is obtained as a white powder by heating arsenic

acid to a moderate temperature. On being more strongly heated it loses oxygen, and passes into arsenic trioxide. When mixed with water it first forms a pasty mass, which is slowly converted into a clear solution of arsenic acid.

Arsenic acid is used in the arts and manufactures as a feeble oxidising agent in the preparation of certain dyes (fuchsin).

The salts of arsenic acid are of slight importance. While those of the alkali metals are readily soluble in water, the other metals mostly form difficultly soluble salts. The magnesium ammonium salt, $MgNH_4AsO_4$, which is formed under similar conditions to the corresponding phosphate (p. 745), and, similarly to it, is used for the determination of arsenic acid, and therefore also of arsenic, deserves to be mentioned. Under the action of reducing substances (filter paper, unburnt coal gas) and on warming, reduction very readily occurs with volatilisation of arsenic, and attention must be paid to this in analysis.

In respect of its electrolytic dissociation, arsenic acid is very similar to phosphoric acid. Even up to a great dilution the aqueous solution contains chiefly the ions H^+ and H_2AsO_4, and the further stages of dissociation are quite subsidiary. At the same concentration, arsenic acid is less dissociated than phosphoric acid, but the difference is not great.

An arsenic pentachloride corresponding to arsenic acid, may be obtained by passing chlorine over arsenic trichloride at ... It forms yellow crystals which melt at ... 40° and can be ... in ether. At a higher temperature it decomposes ... trichloride and chlorine. It is, therefore, much less stable than the corresponding compound of phosphorus, phosphorus pentachloride.

746. **Arsenic Pentasulphide.** A solution of sodium arsenite, Na_3AsO_3, when warmed with sulphur, readily takes up a certain weight of the latter and forms a new salt according to the equation $Na_3AsO_3 + S = Na_3AsO_2S$. We are here dealing with the sodium salt of the arsenate thioarsenate, AsO_2S ...

On attempting to liberate the thioarsenic acid, in the ordinary way by another acid, a yellow precipitate is produced which does ... arsenic trisulphide, but has the composition As_2S_5, and is therefore arsenic pentasulphide. In this process again thioarsenic acid is first formed, but the acid is not stable, and decomposes into arsenic pentasulphide and sulphuretted hydrogen.

Arsenic pentasulphide is also a rather ... compound, and readily decomposes like arsenic trisulphide and sulphur.

747. **Compounds of the Divalent Type.** ...phur and with water to form the compounds they are similar ... belong to a later time that the compounds hitherto discussed.

The simplest compound occurs naturally ... used for ... out is prepared from the two elements by fusing them together, ... technical name is realgar. It fuses readily and passes ...

to arsenic trioxide and sulphur dioxide ; it dissolves in the solvents for arsenic trisulphide leaving behind a residue of arsenic.

Arsenious iodide, AsI_3, is also obtained as a dark-red mass by heating its constituents in a closed tube, and crystallises from carbon disulphide in long needles. In chemical reactions it behaves similarly to the sulphur compound, metallic arsenic being deposited and the corresponding trivalent compounds formed.

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Besides the tetravalent stage of titanium, there also exist a divalent, a trivalent, and a hexavalent stage, but these are of subordinate importance. By heating the vapour of the tetrachloride with hydrogen, the trichloride is obtained in the form of violet scales which dissolve in water, yielding a violet liquid which readily oxidises in the air and deposits titanic acid. These violet solutions can also be obtained from the acid solutions of titanic acid by reduction with zinc or sodium amalgam. They contain, presumably, a violet oxide of trivalent titanium, $Ti^{...}$. With hydrofluoric acid and soluble fluorides salts of a trivalent titanifluoridion, TiF_6, are formed, which are also of a violet colour.

If titanium trichloride is heated alone, it decomposes into tetrachloride, which escapes, and difficultly volatile dichloride which collects in the colder parts of the apparatus as a black crystalline mass volatile at a red heat. The compound reacts violently with water, and yields a yellow-brown solution which oxidises in the air. Compounds of this series are also obtained by the very energetic reduction of the acid titanic solutions with sodium amalgam.

Finally, there is a still higher stage of oxidation of titanium which is obtained when hydrogen peroxide is added to a solution of titanic acid in concentrated sulphuric acid. The liquid immediately becomes deep yellow in colour, and the reaction is visible with such small quantities that it is employed as one of the best methods of detecting hydrogen peroxide. By neutralising the sulphuric acid, a yellow solid substance of the composition TiO_3 can be separated.

747. Titanium Nitride. Titanium exhibits a special tendency to combine with nitrogen. It unites so readily with the latter at moderately high temperatures that most of the preparations which were formerly regarded as metallic titanium consisted chiefly of titanium nitride. A substance with a metallic lustre, which is frequently found in blast furnaces and was formerly regarded as metallic titanium, has been recognised as *titanium cyanide*, $Ti_{10}C_2N_8$. If potassium titanifluoride is reduced with sodium or potassium, the titanium formed at once combines with the nitrogen of the air. Of these nitrogen compounds, which are most easily obtained by heating titanic chloride with ammonia in a red-hot tube, two are known corresponding to the formulae Ti_3N_4 and TiN_2. These are crystalline substances with a metallic lustre, which evolve ammonia copiously on being fused with caustic potash or soda, passing thereby into titanates.

The combining weight of titanium is $Ti = 48.1$.

748. Germanium is an element of extremely rare occurrence. It can be reduced from its oxygen compounds by ignition with carbon or coal, and is thus obtained as a very brittle metal which fuses at about 900° and has the density of 5.5; it is insoluble in dilute acids, is dissolved by aqua regia, and is converted into the dioxide by nitric

hydrogen. Such compounds, more especially with sulphuric acid, are known even in the solid state.

By reducing the pentoxide with hydrogen, or with charcoal at a high temperature, *vanadium trioxide*, V_2O_3, is obtained as a grey-black powder with metallic lustre. This was formerly regarded as metallic vanadium, since, besides having a metallic lustre, it is also a good conductor of electricity. It dissolves in acids to form dark-green salts, containing the trivalent, green trivanadion V''', and which are also obtained by reducing acid solutions of the pentoxide with zinc.

Besides these two oxides, the compounds V_2O, V_2O_2, V_2O_4, and some intermediate compounds have also been prepared. They have all a metallic appearance. The *dioxide* dissolves in dilute acids to form blue liquids, which evolve hydrogen, and have strong reducing properties. They contain, presumably, a divalent, violet blue divanadion V''.

The compounds with the halogens, especially with chlorine, exhibit as great variety as the oxygen compounds. Strange to say, a pentachloride, which would be expected, corresponding to the pentoxide, does not exist; the highest chloride stage is the *tetrachloride*, VCl_4. An oxychloride, however, viz. *vanadyl chloride*, $VOCl_3$(VO = *vanadyl*), belonging to the pentavalent type, is known. It is obtained by first passing hydrogen and then chlorine over a heated mixture of vanadium pentoxide and charcoal. It is a bright yellow liquid, boiling at 127°, which reacts with water with great rise of temperature, and fumes in the air. From this $VOCl_2$ and $VOCl$ are obtained by reduction with hydrogen; they are both solid, crystalline substances, the former being green, the latter brown.

If a mixture of vanadyl trichloride vapour and chlorine is passed over red hot charcoal, the *tetrachloride*, VCl_4, is obtained as a brown liquid, boiling at 154°. On being more strongly heated it decomposes into chlorine and *vanadium trichloride*, VCl_3, which forms lustrous, violet-red crystals, which recall chromic chloride. They attract moisture from the air and deliquesce to a brown liquid. On heating the vapour with hydrogen the tetrachloride is converted into *vanadium dichloride*, VCl_2. This forms apple green, difficultly volatile crystals with a micaceous lustre, which deliquesce in the air to a violet-blue liquid.

Finally, on strongly heating the dichloride in a current of hydrogen, *metallic vanadium* is obtained as an unmelted, grey mass, which acquires a metallic lustre on being rubbed, and does not dissolve in dilute acid. It burns readily in a current of nitrogen, forming *vanadium nitride*, VN, a yellow brown powder with a metallic lustre. On fusion with caustic potash the nitride is converted into vanadic acid with evolution of ammonia.

On passing sulphuretted hydrogen into a solution of ammonium vanadate in ammonia a precipitate is produced which, on continuing to pass the gas, dissolves, forming a fine, violet red coloured liqu

...ording potassium p...
...salt has the composit...
...ortho series.   On add...
...t a brown precipitate...
...he pure vanadium pent...
...ack powder by fusing th...
...te, in its turn, is obtained...
...huretted hydrogen, or, bette...
...t colour, and dissolves in small...
...in excess of sulphur, forms, c...

...catalytically accelerating certain...
...n of aniline to aniline black, wit...
...mployed for that purpose in the...
...p small quantities of the acid ac...
...n.

...dium has been found equal to 51...
...adium are two extremely rare elements...
...pectively 94 and 183.   Free niob...
...the reduction of its chloride with...
...sists the action of dilute acids, has...
...Both elements can be obtained in the...
...metals which melt above 1800, ...
...series, on the side of the base metal...
...a pentoxide, Nb₂O₅, which is the sta...
...the alkali salts of which are decompos...
...recipitation of the hydroxide.   On bein...
...gen the pentoxide passes into a low...
...formerly taken for the metal.
...ecms a penta-chloride which can be obtained...
...with charcoal in a current of chlorine.   It...
...melt at 194 and boil at 240.   If in ho...
...water is not avoided, niobium oxych...
...s a white mass, which does not fuse, but...
...rate is also known, which is deposited on...
...r of the pentachloride.
...ex compounds with fluorine, which exhibit a...
...tion, and which have not yet been arranged...

...tantalum are very similar to those of...
...haracteristic is potassium tantalofluoride, the...
...tantalofluoride, TaF₇, the corresponding...
...formed by dissolving the pentoxide in hydro...

...nd **Indium**.   The elements most nearly related...
...ments are to be found among the alkaline earth...

properties developed to a higher degree than in the case of the allied substances of lower combining weight. It is precipitated from its salts by ammonia or alkalis, and is not soluble in excess of the precipitant. Similarly to the other dioxides of this group it occurs in several forms possessing different degrees of stability; while the freshly prepared, white, gelatinous hydroxide readily dissolves in acids, a difficultly soluble modification is formed on heating. On ignition, the hydroxide passes into the dioxide, ThO_2, which is a white, light powder. This oxide is not soluble in acids except in hot, concentrated sulphuric acid. The oxide obtained by heating the oxalate, on being evaporated with nitric acid or hydrochloric acid, gives a residue which does not dissolve in dilute acid but is soluble in water; the solution is of a colloidal character. This behaviour recalls that of stannic acid (p. 734).

Of the salts, the sulphate and the nitrate are the best known. *Thorium sulphate*, $Th(SO_4)_2$, crystallises according to the temperature with varying amounts of water. These different forms change comparatively slowly into one another, so that it is easy to prepare solutions of one of these forms which are greatly supersaturated for the other forms. To this is due a peculiar behaviour of the sulphate, which is made use of for the purification of the thorium compounds. The anhydrous sulphate, prepared by heating, is dissolved in ice-cold water. A solution is thus produced which is saturated in respect of the anhydrous salt, but greatly supersaturated in respect of a hydrated salt with $4H_2O$. Since, also, the solubility of this latter salt decreases greatly with rising temperature, a solution prepared in the cold with the anhydrous salt will become, on heating, more and more supersaturated in respect of the salt with $4H_2O$, and the spontaneous separation of this hydrate therefore soon occurs. On heating the salt which is deposited until it has lost its water of crystallisation, it again becomes readily soluble in cold water, and behaves as above described.

Thorium nitrate, $Th(NO_3)_4 . 6H_2O$, is a very readily soluble salt, which is obtained by dissolving freshly precipitated thoria in nitric acid. It is used for the preparation of incandescent mantles, a cotton web being moistened with this salt, dried, and heated. The texture burns and the thoria remains as a white, coherent frame-work. By ignition in a Bunsen flame produced under pressure, whereby the material appreciably contracts, the mantles are made ready for use.

The mantles are rendered luminous by being strongly heated in a specially constructed Bunsen flame. It is a remarkable fact that pure thoria gives only a poorly luminous mantle; in order that it may become powerfully luminous small quantities of certain other substances must be added. For this purpose the addition of 1 per cent of cerium oxide (p. 569) has been found to be best. The cause of this influence has not yet been established quite free from doubt, but the most probable view is that the addition effects a catalytic acceleration of the

combustion of the mixture of coal-gas and air in direct contact wit
the skeleton of thoria.   Besides this, the optical properties of thor
appear to be of importance.

The tendency to the formation of complex fluorine salts (cf. p. 73
is greatly diminished in the case of thorium ; thorium fluoride is
precipitate which does not dissolve in excess of hydrofluoric acid, a1
does not therefore exhibit the formation of a hydrothoriofluoric aci
A potassium thoriofluoride, $K_2ThF_6 . 4H_2O$, however, is known as a
almost insoluble crystalline powder.

A very remarkable property of the thorium compounds is, tha
influences are emitted by them which penetrate through solid sub
stances and are characterised by their action on the photographic
plate as well as by the change in the electrical properties of the
air.   We shall enter into these points in greater detail when we
come to discuss uranium, which exhibits these actions in a much
higher degree.

CHAPTER XLII

General.—These three elements resemble chromium in many of their properties, so that they might have been treated in connection with it. On account, however, of their forming thio-acids they so undoubtedly belong to the present class of metals (chromium forms no sulphur compound at all in aqueous solution), that it appears appropriate to separate them from chromium.

The elements *uranium*, *tungsten*, and *molybdenum* are characterised by the fact that their most stable oxygen compounds have the composition MO_3, and are the anhydrides of acids. In accordance with the general rule, the acid properties are least pronounced in the case of the element with the highest combining weight, and become more pronounced as the combining weight decreases.

All three belong to the less frequent elements, although they cannot be characterised as rare. They are difficultly fusible metals, which keep well in the air, but which have found no application in the pure state.

Of all the known elements, uranium has the highest combining weight, viz. $U = 238.5$.

752. Uranium. Uranium was discovered by Klaproth. In the case of *metallic uranium* the same thing happened as in the case of vanadium, viz. the copper-brown coloured dioxide, which is readily formed by the reduction of the higher oxygen compounds, was mistaken for the metal. The true uranium was subsequently obtained by the action of sodium on the chlorine compound; it is a white, difficultly fusible metal, which dissolves fairly readily in dilute acids, and in the potential series stands near cadmium.

Uranium forms a whole series of stages of combination in which it is trivalent to octavalent. The better known and more important compounds are those of the hexavalent and those of the tetravalent type.

By oxidation of the naturally occurring compounds of uranium, salts of uranyl, i.e. of the divalent cation UO_2, are obtained. The

743

normal hydroxide of hexavalent uranium, $U(OH)_6$, has both acid and basic properties. The latter are not sufficiently strongly developed for all the six hydroxyls to be replaceable by acid residues; two, however, can be replaced. In the salts, therefore, there exists the divalent cation $U(OH)_4''$, or its anhydride UO_2'', uranyl, which forms salts like any other divalent cation.

* This occurrence of an "oxygenated metal" has been regarded as something remarkable and extraordinary, but it is readily intelligible when regarded from the point of view that in polyvalent acids and bases, the replacement of hydrion or hydroxidion becomes more difficult the further the replacement proceeds. Just as in aqueous solution phosphoric acid behaves chiefly as a dibasic acid and forms salts of the anion PO_4H'', since those of the anion PO_4''' suffer too great hydrolysis to be present in any considerable quantity, so the hydrolysis of the uranium salts corresponding to the higher cations $U(OH)_5'$, $U(OH)_6$, etc., is too great for these salts to be present in appreciable amount. For even the second cation, $U(OH)_4''$, is so greatly hydrolysed that its salts have a distinctly acid reaction.

Diuranylion, UO_2'', is of a bright yellow colour with green fluorescence, and in the spectroscope exhibits a number of definite absorption bands. Of the salts, the *nitrate* $UO_2(NO_3)_2 \cdot 6H_2O$ is the best known; it forms yellow crystals with green fluorescence, which are readily soluble in water and serve as the starting point in the preparation of other uranium compounds.

From the nitrate, soluble bases precipitate a yellow substance which consists essentially of uranyl hydroxide, $UO_2(OH)_2$ or $U(OH)_6$, but also always contains a quantity of the base in the form of a uranate or salt of uranic acid (*vide infra*). By evaporating a solution of uranyl nitrate in alcohol (in which the alcohol serves to destroy the nitranion) a yellow powder of the composition $UO_2(OH)_2$, free from alkali, is obtained. With other methods of preparation the composition is $U(OH)_6$. This *uranyl hydroxide* dissolves in acids and forms the corresponding, often complex, uranyl salts.

Uranyl has a pronounced tendency to form complex compounds; these are formed with almost all organic acids. Of these the *oxalate*, which is very sensitive to light, and in sunlight evolves gas copiously, is of interest. In this process we do not have an oxidation of the oxalic acid with reduction of the uranyl, but the escaping gas is a mixture of carbon monoxide and carbon dioxide, and a precipitate of uranyl hydroxide is formed at the same time. The oxalic acid therefore undergoes the same decomposition as by heating with elimination of water (p. 446), and the uranium acts catalytically. The uranyl salts of other organic acids exhibit similar decomposition in the light.

With phosphoric acid uranyl forms a *phosphate*, UO_2HPO_4, insoluble in acetic acid, or, in the presence of ammonium salts, the compound $UO_2(NH_4)PO_4$. This precipitation is used for the volumetric

... tetravalent series of ...

... GeO_2 is formed by heating ...
... powder, which, with water, ...
... It dissolves ...
... is also soluble in acid ...
... These salt-like compounds ...

With ... germanium forms ...
... fuming in moist air ...
... water with rise of temper ...
... ("tetrachloride") (cf. p. ...
...gen chloride on metallic ...
tetrachloride, and boils at 72 .

A ... germanium hydride, GeH_4 ...
arsenic hydride. In a heated ...

Germanium fluoride is ...
GeF_4, however, exists, which ...
silicic acid, and forms ...
ficultly soluble in water.

Germanium sulphide, GeS ...
...ses into colloidal ...
ly by a large excess ...
...manion, GeS_2, precip ...
...utions containing ...
is somewhat soluble ...
...talline salts. The ...
l in it germanium ...

Of the compo ...
...phide is the best ...
...manic sulphide ...
...om aqueous ...
...uble in excess ...
...mous sulphide ...

749. Zirconium ...
cate of zircon ...
aproth in ...
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mer, under ...
ible cryst ...
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...ses into ...
y resistant ...
h temper ...
Zirc ...
...avalent ...
...

chlorine an 1 *tetrachloride*.   The latter forms dark-green cry-tals, which dissolve in water to form a dark-green solution ; regarding the latter, it has been stated that it is not of itself oxidised by the atmospheric oxygen, but is so in presence of iron salts   This is apparently another case of catalytic acceleration.

From the tetrachloride, a *trichloride*, UCl_3, can be obtained by reduction with hydrogen ; this is a brown-red mass which readily dissolves in water, but with the latter forthwith evolves hydrogen and passes into a basic chloride of tetravalent uranium.   The fresh solution gives with caustic potash a brown precipitate of *uranium hydroxide* which also very quickly oxidises with evolution of hydrogen.

754. **Sulphur Compounds.**—Ammonium sulphide deposits a brown precipitate from uranyl salts ; the precipitate is *uranyl sulphide*, UO_2S, which is, however, partially decomposed.   For from the sulphur compound even water splits off sulphuretted hydrogen, which partially reduces the uranic oxide formed, and is converted into sulphur.

755. **Uranium Rays and Radio-active Substances.**—In the case of uranium a property was first observed which, however, has since been found in varying degree in other elements also, and in their compounds ; it consists in the following.   If any uranium compound is placed on a photographic plate covered with black paper, the plate undergoes a change as if light had acted on it, *i.e.* it can be developed (p. 690).   This action takes place also through thin plates of mica or of glass, but is diminished by plates of greater thickness proportionately with their density and thickness.

A further influence emitted by these substances is that they make the air and other gases electrically *conductive*, so that an electric current can be passed through them.   This property serves best for the measurement of the influence exercised.

Finally, certain phosphorescent substances, more especially barium platinocyanide (p. 765), are rendered luminous by this action ; but this effect becomes visible only with fairly high degrees of activity.

It has been found that these processes are due to certain material changes in the particular substances, in which large amounts of energy are developed.   This energy assumes, in the first instance, the form of "radiations," *i.e.* it is propagated through space with very great velocity, and essentially in straight lines   Its propagation is influenced by the presence of bodies only in so far as these absorb a definite portion of the energy which is finally changed into heat.   This transformation is, in the first degree, proportional to the mass (density × thickness) of the substances through which the radiation passes and is independent of their chemical nature.   For the rest, the radiations themselves are made up of different parts, which are distinguished from each other by, amongst other things, their power of being absorbed.   Whereas some are retained even by thin paper, others

can penetrate through thick steel plates. Radiations having to a certain extent a similar behaviour are known as "cathode rays," which are produced from the cathode when electrical discharges occur in very dilute gases; from the anode also, similar rays proceed. The chemical radiations of the substances above mentioned, which are called radio-active substances, can be characterised as follows —

A portion, and that the greatest (when measured by the amount of energy involved), possesses in only a very slight degree the power of penetrating ponderable substances; and in a magnetic field it is deviated from its straight course in the same direction as a current of positive electricity. These rays are designated as α-rays. Besides these there are β-rays, which are more penetrating, are deviated by a magnet in the same direction as a current of negative electricity, and are photographically active. Finally, there are also γ-rays, which behave like the X-rays discovered by Röntgen, are very penetrating, and experience no deviation in the magnetic field. The investigations so far carried out, refer chiefly to the α-rays, the strength of which is measured by the conductivity which they impart to the air.

This property of imparting conductivity to the air by means of their α-rays, is possessed, in the first place, by all uranium compounds, in a measure nearly proportional to the amount of uranium present, and nearly independent of the temperature and other circumstances. It is also met with in the case of the thorium compounds. The property can, it is true, be temporarily altered, but again appears after some time in its former strength; and is, in the end, quite independent of the treatment which the preparation has meanwhile undergone.

In the case of various minerals containing uranium and thorium, the radiation was found considerably more intense than in the pure specimens of these elements. This led to the search for other substances possessing a correspondingly greater radiation; and various names, such as polonium, actinium, radio-tellurium, have been proposed for these powerfully radiating substances. Although it is undoubted that several such elements do really exist, only one of these has been isolated in any degree of purity, and characterised, namely, radium, discovered by M. and Mme. Curie.

Radium is an element of the alkaline earth group. In its properties it is so closely related to barium, that it can be separated from it only by approximate methods (fractional crystallisation of the bromides). It differs from barium, firstly, in its exceedingly intense radiation; and, secondly, in its spectrum. It imparts a red coloration to the flame of the Bunsen burner, whereas barium gives a green colour. It is not yet known in the metallic state, since it occurs in the minerals above mentioned only in exceedingly minute amounts. Its combining weight is Ra = 225.

The most remarkable property of radium, which it possesses in all

its compounds, is that of continuously developing energy, which makes its appearance, in the first place, in the form of radiations already described; but when these are retained by thick casings of metal it is transformed into heat. One gram of radium develops in an hour about 100 cal. or 418 joules; or in a second, something over one million ergs. Since an external source of this energy could not be demonstrated, it appeared as if the law of the conservation of energy was disobeyed, until it was discovered by Ramsay and Soddy that *helium* is produced from the radium salt in amount proportional to the energy developed. It may be assumed, therefore, that we have here a case of true transmutation, such as the alchemists, in vain, attempted to bring about, that is to say, we have here a case of the transmutation of one element into another. There is no contradiction in the fact that this hitherto unknown reaction is associated with a greater development of energy than usual, amounting to some million times more than that which is developed in the formation of water from an amount of detonating gas equivalent to the helium produced. A diminution in the weight of radium has so far not been observed. From probable assumptions, it can be calculated that the "average life," *i.e.* the reciprocal of the fractional amount changed in a second, amounts, in the case of radium, to about 1500 years, so that a measurable diminution in weight could be observed only by testing fairly large amounts of radium over a period of several years.

Helium is not the immediate product of the spontaneous transmutation of radium, but intermediate substances of greatly inferior stability are formed. These behave, in general, like elementary gases of the type of argon and helium. They are called emanations. The emanation from radium has a molar weight of about 160 (judged from diffusion experiments); can be condensed at the temperature of liquid air; possesses its own spectrum, having the character of the helium spectrum; but has an average life of only 128 hours. In its turn formation it gives rise to other similar substances of still less stability, so that, on the whole, about five different stages are passed through, which differ in their life. Uranium and thorium behave similarly.

These facts lead to the assumption that the well-known elements uranium and thorium have only a transitory existence, and are undergoing spontaneous transmutation with evolution of energy. The final product of their transformation appears to be helium, for this is always found in the minerals in which these two elements occur. On comparing the intensity of their radiation with that of radium and of the emanation, the conclusion is reached that their average life must be very great, in round numbers, a thousand million years.[1] This can

[1] Not infrequently the remark is heard, that if this process had been going on from eternity, it must already have come to an end. There has to be noted, in reply to this, that the conception of a limit has no sense if phenomena, starting from the limits of what has been known hitherto, are referred in the other direction; the present is the limit at every point.

ater than that assumed by geologists for the development of the

56. **Tungsten**. —This element was discovered in 1781 by
le.   Metallic tungsten can be obtained by the reduction of its
in a current of hydrogen or with charcoal; it is a grey, very
tly fusible, hard metal, the density of which is 16.   On account
se two properties it would be very suitable for cannon balls if its
ult fusibility did not act as a hindrance to its manipulation.   It
technical application as an addition to steel (tungsten steel).
he combining weight is $W = 184$
ungsten forms many compounds in which it appears as divalent
exavalent.   The lower stages have basic properties; the highest
a compound is a pronounced acid anhydride.   Of all the stages,
the most stable.
ungsten trioxide, WO_3, the anhydride of tungstic acid, is obtained
yellow powder by the action of acids on its salts, some of which
naturally; it is very slightly soluble in water, but readily dis
in alkalis.   According to the temperature of precipitation, there
ained the anhydride (in the heat) or the hydroxides $WO(OH)_4$
$WO_2(OH)_2$.
y dissolving the oxide or hydroxide in the calculated amount of
le potash or caustic soda solution, and evaporating to the point
ystallisation, the normal tungstates K_2WO_4 and Na_2WO_4 are
ned in hydrated crystals.   These pass, however, with extreme
into salts of more complex composition, the tungstic acid forming
nsed acids, which partly crystallise out with the normal tung-
as double salts.
ormal tungstates occur in nature, and constitute the ores of
ten.   The ferrous compound, $FeWO_4$ (which generally contains
anese), is called wolfram; the calcium compound, $CaWO_4$, scheelite
d salt, scheelite

n boiling a solution of an alkali tungstate with excess of trioxide,
quantities of the latter are dissolved, and the metatungstates,
WO_{12} are formed in which a very stable condensed tungstanion,
, is present, the reactions of which differ entirely from those
mal tungstanion, WO_4.   For example, the dissolved salts are
recipitated by acids.   By the action of sulphuric acid on the
ltly soluble barium salt, a solution of metatungstic acid can be
ned, from which the latter can be obtained in yellow, extremely
le crystals, by evaporation.
ifferent from metatungstic acid, there is the so-called colloidal
tic acid, which is obtained by dialysing a solution of a normal
state slightly acidified with hydrochloric acid.   The liquid dries
a gummy mass, which redissolves in water, forming a sticky
; it does not taste acid, and is not precipitated from solution by
r other substances, as happens in the case of colloids.   The solu

tion also exhibits an appreciable depression of the freezing point which leads to the (doubtful) formula $H_4W_5O_{10}$.

Besides the above, other diversities have also been observed in the case of tungstic acid, depending on the very ready and often occurring formation of complex acids with other acids. The compounds with silicic acid have been most thoroughly investigated; similar compounds with phosphoric, arsenic, vanadic, niobic, boric, and other acids also exist. The composition is that of the above acids plus a definite generally a larger number of combining weights of WO_3, in the process, the basicity of the other acids generally remains unchanged, but the complex acids produced are mostly considerably stronger than the mother substances. A description of the different compounds would take us too far.

On treating tungstates with zinc in acid solution, the fluid becomes dark blue, and on further reduction brown. It then contains the tetravalent ion W''''. From this, tungstanion is again readily formed by means of oxidising agents.

Very varied compounds of the general formula $Na_m(WO)_n$, are obtained by weak reduction of sodium tungstate (by fusion with a ...; these have all a fine metallic lustre, have different colour according to the amount of tungsten they contain, conduct electricity like a metal, and are extremely resistant to the action of water, acids, and bases. They find an application as "tungsten bronze."

757. Chlorides of Tungsten.—On heating metallic tungsten in a current of chlorine, with careful exclusion of oxygen, the *tungsten hexachloride*, WCl_6, is obtained in black-violet crystals, which melt at 275 and boil at 347. The vapour contains a little free chlorine, so that on repeated distillation chlorine escapes, and the lower stage, *tungsten pentachloride*, WCl_5, is formed in black-green crystalline needles, which melt at 248 and boil at 276. This substance also readily splits off chlorine, and on distillation in a current of an indifferent gas leaves a residue of tungsten tetrachloride, WCl_4, as a non-volatile, grey-brown mass. By the action of reducing agents, e.g. of hydrogen, this compound finally passes into the dichloride, WCl_2, which has a similar appearance.

Besides these compounds, the oxychlorides, viz. $WOCl_4$ and WO_2Cl_2, are very readily formed in the presence of oxygen or water. The first compound forms long, dark red needles, melting at 210 and boiling at 228; the second, which is comparable with chromyl chloride, appears in bright yellow laminæ, the melting point of which lies above the temperature of sublimation (about 260). On distillation it readily decomposes into the preceding compound and a residue of tungsten trioxide. Both undergo violent decomposition with water, forming tungstic acid and hydrogen chloride.

758. Sulphur Compounds. The acid-forming properties of tungsten are exhibited also by its sulphur compounds, for it forms

thiotungstates in which the oxygen of the tungstates is gradually replaced by sulphur.

By passing sulphuretted hydrogen into a solution of an alkali tungstate, the corresponding thiotungstate, M_2WS_4, is obtained only when there is excess of alkali hydrosulphide. If no excess is present, on dilution with water the sulphur in the thio-acid is gradually replaced by oxygen, sulphuretted hydrogen being evolved. Thiotungstic anion is yellow in colour; by replacing the sulphur with oxygen, the anion becomes correspondingly paler.

On adding acids to the thiotungstates, tungsten sulphide is precipitated, and sulphuretted hydrogen is evolved, thiotungstic acid, which is primarily formed, decomposing as usual into these components. Tungsten trisulphide is thus obtained as a brown, amorphous precipitate which passes into colloidal solution in water.

From tungsten and sulphur at a high temperature, a lower sulphide, WS_2, is obtained in grey, graphite-like laminae, which are very stable.

759. Molybdenum.—The chemical individuality of molybdenum, like that of tungsten, was established by Scheele, although the metal was not obtained till later.

Molybdenum resembles the related elements in respect of the variety of its compounds, for its valency varies from two to six. In this case also, the compounds of the hexavalent type are the most stable.

The combining weight of molybdenum is 96 0.

Metallic molybdenum is obtained as a white, very difficultly fusible metal which, like iron, becomes more readily fusible and very hard through absorption of carbon. It is not attacked by dilute acids and is oxidised by nitric acid. In the potential series, it appears to stand in the neighbourhood of lead.

760. Molybdenum Trioxide, the anhydride of molybdic acid, is obtained in the crude state by roasting the naturally occurring molybdenum sulphide, and is purified by dissolving in ammonia and repeated roasting. It is a white substance which becomes yellow on heating; at a red heat it melts and volatilises. It is readily reduced to the metal by means of hydrogen and charcoal.

Molybdenum trioxide is the anhydride of a series of acids which are formed from it and the elements of water in varying proportions. Whereas in the case of tungstic acid the metatungstic acid at least was found to be well characterised and stable, no similar compound is known in the present case, but the different polymolybdic acids appear to pass quickly and readily into one another. Compounds of trimolybdic acid, $H_2Mo_3O_{10}$, are the most frequent.

The power of forming complex acids is here developed to a particularly high degree, and molybdenum trioxide appears to unite with practically all other acids to form such compounds. For while pure

molybdenum trioxide, or its hydrate, is only sparingly soluble in water, it passes abundantly into solution in free acids; salts of molybdic acid therefore give no precipitate of molybdic acid on adding excess of another acid.

Of these complex compounds the phosphomolybdic acid $H_3PO_4 . 10MoO_3$ is the best known. Besides the compound with $10MoO_3$ there are also compounds with perfectly similar properties containing $11MoO_3$ and $12MoO_3$.

The very difficultly soluble ammonium salt of these acids is obtained by warming an acid solution of ammonium molybdate with a liquid containing phosphoric acid. The liquid first becomes yellow, and then deposits a yellow powder, which is the above ammonium salt. As is frequently the case in the formation of complex compounds, the reaction does not take place instantaneously, but requires a moderately long time for its completion.

* Since the reaction occurs in acid solution, and since a very large quantity of precipitate is obtained for a small quantity of phosphoric acid, the reaction is employed for the detection of phosphoric acid in analysis. Care must be taken that the molybdic acid is present in excess as, otherwise, soluble compounds can be formed.

From the ammonium salt the free *phosphomolybdic acid* can be obtained by warming with aqua regia, whereby the ammonia is destroyed with evolution of nitrogen. The solution on concentration yields fine crystals of the free acid. It can also be obtained by warming phosphoric acid and molybdic acid in the requisite proportions. Pyro- and meta-phosphoric acids do not give these compounds. This free acid is yellow, very readily soluble in water, and yields precipitates with "alkaloids" (organic compounds, basic derivatives of ammonia which occur in plants and have mostly a powerful physiological action); it serves therefore as a reagent for these

761 Lower Oxygen Compounds.—If zinc is introduced into an acid solution of molybdic acid, the liquid first becomes blue, and on further reduction passes through various colours into brown. The solution then contains a salt of the trivalent molybdenum Mo   by very powerful reduction one can descend still lower; the resulting solution, however, oxidises with extreme readiness.

From molybdenum trioxide, the corresponding *sesquioxide*, Mo_2O_3, is obtained as a black powder by reduction with hydrogen at a red heat. If the temperature is only moderately high, the dioxide MoO_2 is formed as a crystalline, violet, or copper-coloured mass. Between this and the trioxide are the readily formed blue compounds the composition of which varies and cannot be characterised with sufficient sharpness.

762 Chlorine Compounds of Molybdenum.—A chloride corresponding to molybdenum trioxide is not known. the highest chlorine stage is a *pentachloride*, $MoCl_5$. This is obtained by gently warming

ic molybdenum in a current of chlorine ; it is a dark red vapour,
condenses to a liquid, boiling at 268 and solidifying at 194 to
green crystals.   The chloride reacts violently with water and
a blue liquid which deposits a brown precipitate of molybdenum
ydroxide on addition of alkalis, while a molybdate remains in
on.

hen the pentachloride is carefully heated in a current of hydrogen,
es into *molybdenum trichloride*, which is very similar in appear-
to red phosphorus.   On being more strongly heated, this de-
es into difficultly volatile *dichloride*, which remains behind, and
loride, which volatilises.   The former is a yellow, non-crystalline
the latter a brown powder.   All the chlorides react energetically
ndergo double decomposition with water

sides the chlorides, there are also a number of *oxychlorides*,
of which are very readily formed.   The compound MoO_2Cl_2 is
-white in colour, and is obtained by heating a mixture of molyb-
trioxide and charcoal in a current of chlorine.   Besides it
are also formed the violet compound $Mo_2O_3Cl_6$, and the green
Cl_2, which become more volatile as the amount of chlorine
es , the compound last mentioned volatilises even under 100 .
olybdenum trioxide volatilises very readily at 150 -200 in a
t of chlorine , this is due to the formation of a compound :
$O_2Cl_2 = MoO_3 + 2HCl$.   Salts of molybdic acid are also de-
ed, the molybdic acid escaping and a chloride of the particular
remaining behind.

3 Sulphur Compounds. — In nature the compound MoS,
as *molybdenum glance*.   It is a grey-black substance, similar to
ite, and is the source from which the other molybdenum com-
s are obtained.

passing sulphuretted hydrogen into the solutions of the alkali
dates, the liquid becomes intense red brown in colour and
as a corresponding *thiomolybdate*.   A similar variety to that
by the salts of molybdic acid is found also in the case of the
f thiomolybdic acid, with respect to the relation between acid
se, so that the description of the different compounds would
o far.   On adding an acid to the solutions, a precipitate of
denum trisulphide is formed with evolution of sulphuretted
gen , it is a red brown substance, which gives a colloidal solution
ure water

CHAPTER XLIII

GOLD AND THE PLATINUM METALS

764. General.—The metals which have to be treated in this chapter constitute, along with silver, the group of the *noble metals*. By this designation there is understood metals which do not unite with the oxygen of the air either at high or low temperatures, and which can be converted only with difficulty into compounds by means of chemical reactions. In other words, they are metallic elements which in the elementary state contain much less free energy than their compounds.

Such a statement cannot of course be made quite general, since it depends on the nature of the compounds what difference of energy exists between their free energy and that of their components. Thus, in fact, we see that towards certain reagents the noble metals behave as base, *i.e.* pass spontaneously into compounds. The reagents which have this action on the noble metals are chiefly those by which the metals are converted into *complex* compounds.

Of the elements grouped together in this chapter, *gold* occupies a rather solitary position, while the six *platinum metals* form a well-arranged group of three pairs. This is seen from the following table, in which the neighbouring elements are especially similar to each another. The chemical similarity follows the values of the combining weights :—

Palladium	.	.	106·5	Platinum	.	.	194·8
Rhodium	.	.	103·0	Iridium	.	.	193·0
Ruthenium	.	.	101·7	Osmium	.	.	191

765. Gold.—The element gold occurs in nature almost entirely in the metallic state; in spite of its rarity it may, by reason of its remarkable properties, be regarded as that element which has been longest known and which was earliest used.

Gold is a lustrous, yellow metal, whose density is 19·3, and which melts at 1035 . In the air, it remains unchanged at all temperatures; moisture also has no influence on its lustre. By reason of its in-

erability it has been used from olden times as a standard of value
d for enabling this standard to be preserved. At the present day it
been adopted by most countries as the basis of their coinage.

Gold is not attacked by dilute or concentrated acids, so that it
mains as a residue (as a brown powder) when auriferous metal is
ated with nitric acid or with concentrated sulphuric acid, which has
similar action. On the other hand, it dissolves fairly readily in
lorine water and in other liquids which give off free chlorine. A
ixture of nitric and hydrochloric acids has the latter property
357), and is used under the name of " aqua regia " (since it dissolves
king of the metals) for the preparation of gold compounds.

Of the mechanical properties of gold its malleability is the chief ;
is allows of the metal being rolled or beaten out to extremely thin
ves. These leaves transmit green light. Still thinner films of gold
obtained by chemical precipitation from solution. Finely divided
ld, such as is obtained by reduction on the skin when this is
istened with gold solution, appears red violet. This property is
ade use of in photography for the purpose of imparting the well-
own brown-violet "photographic tint" to the brown positives,
sisting of finely divided silver (p. 687). For this purpose the
tures are treated with a very dilute, neutral or alkaline solution
gold, whereby the gold is precipitated by the metallic silver of the
ture, while the silver passes into the corresponding compound.

Gold which is precipitated from solution in a very finely divided
dition, generally appears blue by transmitted light, while the
ident light is dispersed with a brown colour. If, however, pre-
itation takes place in a very diluted condition, purple red solutions
colloidal gold are obtained ; these are precipitated by salts and
ibit the general properties of colloidal solutions.

* The simplest means of obtaining such solutions consists in
owing an electric arc to pass between electrodes of gold under
ter to which a trace of alkali has been added

In fused glass also, gold dissolves in a colloidal condition and yields
fine red-coloured *gold ruby glass*. Finally, a solid solution of colloidal
ld in stannic acid, obtained by the precipitation of gold solutions
th stannous chloride, has long been known by the name of *purple of*
sius, and is employed in porcelain painting.

The combining weight of gold is Au = 197·2.

766. **Gold Compounds**.—Regarding the ions formed by gold
re is as yet no sufficient knowledge. It is known that gold acts
th as a mono- and as a tri-valent element ; in the solutions also of
trivalent compounds, trivalent triaurion, Au``, can be assumed (the
novalent gold compounds are not appreciably soluble in water) ; it
however, unknown in what proportion these solutions contain the
Au`` along with other complex ions, such as gold forms with ease
in considerable numbers.

The best known gold compound is *gold chloride*, which is formed on dissolving gold in aqua regia. A yellow solution is produced from which *hydroaurichloric acid*, $HAuCl_4$, can be obtained in yellow, readily soluble crystals, by careful evaporation. On heating somewhat more strongly, hydrogen chloride escapes and *gold trichloride*, $AuCl_3$, remains behind as a brown, crystalline mass which is also readily soluble. Its aqueous solution has an acid reaction and contains the gold in the form of a complex anion of the composition $AuOCl_2'$, for the trichloride unites with the solvent water to form the compound H_2AuOCl_3, which partially dissociates into its ions. By no means all the gold chloride however, appears to undergo this transformation.

The *hydroaurichloric acid*, $HAuCl_4$, is much better characterised. A large number of well-crystallised salts of the anion $AuCl_4'$ are known which, however, are generally designated as "gold chloride double salts." They are obtained by the action of the solution of hydrochloroauric acid on any salts of the particular base, best on the chlorides; they are often used for the characterisation of organic bases.

Of the salts of aurichloridion, $AuCl_4'$, the *potassium salt* has to be mentioned which, according to the conditions of crystallisation crystallises with varying amounts of water (over sulphuric acid in anhydrous crystals); also the sodium salt $NaAuCl_4 . 2H_2O$, which is employed as "gold salt" in photography (p. 755).

Strong bases decompose both the trichloride and the hydroaurichloric acid, and a yellow brown precipitate of (impure) auric hydroxide, $Au(OH)_3$, is formed; this is soluble in excess of the base since the hydroxide has weak acid properties. The *potassium aurate*, $KAuO_2$, which is formed under these conditions has also been obtained in the solid state as a bright coloured salt, from which metallic gold is very readily precipitated (*e.g.* by dust).

By precipitating gold chloride with baryta, difficultly soluble *barium aurate* is obtained which leaves a residue of fairly pure gold hydroxide on being treated with dilute nitric acid. This hydroxide does not dissolve in dilute acids but does so in concentrated nitric acid, with which it forms an aurinitric acid similar to hydroaurichloric acid. Gold trihydroxide must therefore be regarded as an essential basic hydroxide.

From solutions of gold, reducing agents of all kinds, *e.g.* ferrous salts, sulphurous acid, oxalic acid, etc., precipitate metallic gold, which, according to the conditions of experiment, appears as a yellow precipitate of metallic lustre or as a brown powder. The commencement of the separation is always signalised by the solutions assuming a blue coloration by transmitted light.

767. **Aurous Chloride** — By carefully heating gold chloride to 180°, the compound $AuCl$ is obtained according to the equation: $AuCl_3 = AuCl + Cl_2$. It is a yellow-white powder, which does not dissolve in water but decomposes according to the equation:

AuCl AnCl$_3$ + 2Au, into gold trichloride, which dissolves, and metallic gold, which remains behind. Aurous chloride forms with the alkali chlorides complex salts, which can be derived from an auro-chlor-ion, AuCl$_2$'. They are obtained by carefully heating the corre-sponding auric compounds; on solution in water, however, these salts undergo the same decomposition as aurous chloride.

768 Sulphur Compounds.—On account of the reducing action of sulphuretted hydrogen, the sulphur compounds of the aurous series are more stable and more easily prepared than those of the auric series. Aurous sulphide, Au$_2$S, is obtained (mixed with sulphur) by passing sulphuretted hydrogen into a boiling solution of gold chloride. It is a dark precipitate which yields a brown colloidal solution with pure water. The solution does not exhibit the reactions of a sulphide, and therefore contains only a negligible amount of iron.

Aurous sulphide unites with alkali sulphides to form thio-salts of the formula MAuS, which are soluble in water but are quickly decomposed in the air owing to oxidation. By fusion with alkali sulphides, therefore, gold is rendered soluble owing to the formation of the above compounds. They are immediately decomposed by acids.

On treating a solution of gold chloride in the cold with sulphur-etted hydrogen, a more highly sulphuretted compound of gold, having approximately the composition AuS or Au$_2$S$_3$, is precipitated. It is a black amorphous mass which decomposes into gold and sulphur on being heated, is insoluble in acids, and can be brought into colloidal solution by treating with potassium cyanide and then with pure water. This precipitate dissolves in yellow but not in colourless ammonium sulphide, with formation of *ammonium thioaurate*, NH$_4$AuS$_2$.

769 Complex Gold Compounds.—As is evident from the description of the more simple gold compounds, the saline derivatives of gold are chiefly of a complex character, *i.e.* the gold is not present in them as an elementary ion. Besides these there also exist a large number of other complex gold compounds; such compounds are formed with especial readiness with cyanogen and sulphur.

The gold compounds are for the most part readily soluble in potas-sium cyanide, and give rise chiefly to two series of salts, the aurous and the auric cyanides. The former are derived from *aurocyanidion*, Au(CN)$_2$', which corresponds to argenticyanidion, and are formed by dissolving aurous compounds in alkali cyanides. The compounds of the second series are the salts of *auricyanidion*, Au(CN)$_4$', and are formed from auric compounds and cyanides; they are the better known and the more important of the two classes.

In neither case have the free acids been prepared, but a number of salts are known. These are colourless; they do not exhibit the ordinary reactions of gold, and are, for example, not nearly so readily reduced as these.

The potassium salt, $KAu(CN)_4$, crystallises with $1\frac{1}{2}H_2O$ in colourless, readily soluble plates, and has a technical importance in two different directions. On the one hand, it is used for the electro-gilding of other metals. For this purpose it has the same advantages as are possessed by potassium argenticyanide for silvering (p. 691). As a rule, it is not first prepared specially, but potassium cyanide is electrolysed between gold electrodes until a sufficient amount of the substance has been formed in the bath. Its formation takes place at the anode where cyanogen is liberated from the potassium cyanide; the former immediately yields gold cyanide with the gold, which then dissolves in the excess of potassium cyanide with formation of potassium auricyanide. At the same time, hydrogen is liberated and caustic potash is formed at the cathode; the latter must be removed by addition of acid.

Another application depends on the fact that metallic gold dissolves in a dilute solution of potassium cyanide, with co-operation of the atmospheric oxygen, to form potassium auricyanide, according to the equation: $2Au + 8KCN + 2O_2 + 4H_2O = 2KAu(CN)_4 + 6KOH + H_2O_2$. As can be seen from the equation, caustic potash and hydrogen peroxide are formed besides the gold salt. It has already been mentioned that the formation of the peroxide in oxidations by means of free oxygen is a frequent phenomenon (p. 160). The above reaction is made use of on the large scale for the extraction of gold in those cases where it occurs so finely divided that levigation or amalgamation cannot be successfully employed (*vide infra*). South African gold, more especially, is obtained in this way. The gold is again separated by electrolysis from the solutions (for which very dilute potassium cyanide must be employed).

Gold therefore behaves as a base metal towards the solution of potassium cyanide, for it dissolves in it under the joint action of the atmospheric oxygen, in much the same way as copper dissolves in hydrochloric acid under the influence of the air. This is due to its passing into a complex compound in which the concentration of elementary aurion is extremely small. It has already been pointed out that the smaller the concentration of the metal ion in the resulting solution, the more does the metal behave as a base metal towards that reagent (p. 695). This refers not only to the electrical behaviour, for this is only an expression of the chemical properties, but to all chemical processes.

These relations can be interpreted in the following general manner. As has already been frequently emphasised, every possible substance has a tendency to formation, and this is all the greater the smaller its concentration at that point where it could be formed. Of a necessity, therefore, under given conditions, traces of every possible substance must be formed. The noble metals, now, are those for which unmeasurably small concentrations of their ions suffice to counterac-

he tendency to further ion-formation. For this reason gold appears insoluble in the ordinary acids. If, however, the conditions are such that even these minute amounts of ions disappear by being used up in the formation of complex compounds, more gold must pass into solution, and this must continue until the concentration of aurion necessary for equilibrium has been established in the solution. A noble metal, therefore, will appear as base only in those solutions with the components of which it forms complexes, and it will appear all the more base the more stable these complexes are in respect of the metal ion, or the less the amount of metal ion split off by the complex at a given, absolute concentration. This view has been universally confirmed by experience.

We find here the explanation of the solubility of gold in aqua regia, although gold is not (or rather, is only slightly) soluble in nitric acid. The hydroaurichloric acid which is formed is a comparatively stable complex compound in whose solution the concentration of aurion is only very small, while the solution in nitric acid contains more gold and is less stable. Aqua regia, therefore, dissolves gold not because it is a stronger oxidising agent than nitric acid, but because gold is a less noble metal with respect to aqua regia than with respect to nitric acid. It is still less noble towards potassium cyanide solution and free oxygen, which are in themselves no very effective oxidising agents.

Gold also forms complex compounds with substances containing *sulphur*. The simple thio-acids of gold have already been mentioned. We have still to mention the complex compound which gold forms with the thiosulphates. By the action of a solution of sodium thiosulphate on neutral gold chloride, a salt of the composition $Na_3Au(S_2O_3)_2$ is obtained; it can be precipitated from the solution by the addition of alcohol, has a sweet taste, and does not exhibit the reactions of the ordinary solutions of gold salts. The corresponding aurithiosulphuric acid, $H_3Au(S_2O_3)_2$, can also be prepared by decomposing the barium salt (obtained in a similar manner to the potassium salt).

These compounds play a rôle in the "toning" of positive silver pictures in photography, as they are contained in the combined toning and fixing solutions.

770. **Metallurgy of Gold.** Since by far the largest amount of gold occurs in the metallic state, the metallurgy of gold was for long a *mechanical* and not a chemical operation. The auriferous sand was treated with running water which carried away the light sand but left the heavy grains of gold behind. If the gold was not contained in sand but in the solid rock (e.g. in quartz), this operation had to be preceded by a mechanical disintegration of the rock, unless it was preferred to fuse the whole stone, with suitable additions, whereby the gold, being the densest component, sank to the bottom.

Gold, however, frequently occurs in such a fine state of division that it is carried away in the process of levigation. In these cases it can be extracted with mercury, in which it is readily soluble ; the mercury is recovered by distillation.

Still more finely divided gold is extracted with a very dilute solution of potassium cyanide (p. 758).

Metallic gold is not employed in the pure state for coinage and articles of jewellery, as it is too soft, but at most is used in the laboratory for caustic alkali fusions, because it is more resistant to caustic potash and soda in the heat than is platinum or silver. For ordinary usage, gold is alloyed with other metals, generally copper. The amount of gold contained in the alloy for coinage is regulated by Government: English gold coinage contains 91 66 per cent of gold.

771. **Platinum.**—Of the six metals of the platinum group mentioned above (p. 754) *platinum* itself is the most frequent and the most important. Like gold it occurs native and is obtained by levigation. Crude "platinum ore" contains all six metals in varying amounts, and must be subjected to a rather complicated process of separation in order that the components may be obtained in the pure state.

Platinum is a grey-white metal having a density 21 4, and melting at 1770. It can be welded at a bright red heat, can be drawn to a fine wire, and possesses great resistibility to chemical influences. It is, more especially, not appreciably dissolved by pure acids ; its durability under the action of boiling sulphuric acid has already been mentioned (p. 289). It is dissolved by aqua regia, but also rather slowly. It is also fairly stable to electrolytically liberated chlorine. It is attacked, however, in cases where it can combine at a red heat with phosphorus ; many a platinum crucible has been eaten through by igniting phosphates along with carbon. Platinum is also attacked by melting caustic potash or soda, while the alkali carbonates can be fused without danger in platinum vessels. On being heated for a long time in contact with carbon, the platinum absorbs some of it, and becomes brittle. It mixes with readily reducible metals, and forms easily fusible alloys ; such metals, therefore, must not come into contact with hot platinum vessels. It is indifferent towards hydrofluoric acid.

These properties render platinum of great value both in the laboratory and in the arts ; indeed, so much of the metal is used in the latter, that its price has risen to several times its former value.

In the laboratory platinum is used for the most varied purposes in the form of crucibles, dishes, wire, and foil, especially for exact analysis. In the arts it was formerly chiefly used for concentration retorts in the sulphuric acid manufacture. On account of the change to the anhydride process now taking place in the sulphuric acid manufacture (p. 280), the platinum does not become free, for the new process also requires platinum, although for other purposes. In commercial electrolysis also, electrodes of platinum are often used.

A widely extended application of platinum is due to the fact that its coefficient of expansion is almost the same as that of glass. Platinum wires are, therefore, employed for leading electric conductors air-tight through glass.   Whereas, formerly, use was made of this only in scientific apparatus, large quantities of platinum are now used for the conducting junctions in electrical incandescent lamps, the interior of which must be exhausted.   Further, much platinum is used in electrotechnics for coating electrical contacts, since the platinum surfaces are not oxidised by the sparks which are there formed, and therefore retain their conductivity.

On account of its high melting point, platinum does not fuse in ordinary flames, not even in the hottest part of the Bunsen flame.   It can be readily fused, however, in the oxyhydrogen flame (p. 102), and this is used in the arts on a large scale for the purpose of fusing platinum to a mass ; the crucible material is made of burnt lime.

Since most of the platinum compounds decompose at a red heat, leaving a residue of metallic platinum, the latter is in this way obtained as an unfused, finely divided mass, known as *platinum sponge*.   In this form platinum exhibits very pronounced catalytic properties, chiefly in the acceleration of numerous gas reactions.   Several examples of this have already been given , the most important, technically, is the preparation of sulphur trioxide by means of spongy platinum.   It must, however, be emphasised that such catalysers show by no means a uniform behaviour in accelerating all slowly occurring reactions.   On the contrary, so far as yet known, the relationship between reaction and catalyser is an *individual* one.

* Spongy platinum was used by Döbereiner, the discoverer of the above property, for the construction of the lamp named after him, which was greatly used at the time of its discovery (1823), when matches did not exist.   It depends on the fact that a current of hydrogen gas, when caused to strike on a piece of spongy platinum, ignites under its influence so quickly with the atmospheric oxygen that the metal becomes red-hot and ignites the hydrogen   The Döbereiner lamp, therefore, consists of an automatic hydrogen generator (the arrangement of which is seen from Fig. 125), filled with zinc and sulphuric acid, and of a piece of platinum sponge placed in a small box opposite the exit tap.   In recent times, the same

Fig. 12

principle has been employed for the ignition of gas flames by the mere opening of the tap, especially in the case of incandescent burners.

Since the catalytic actions of platinum take place at its surface, they
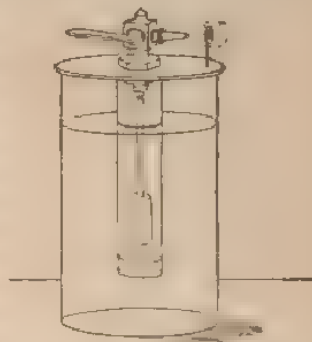
are, for a given amount of metal, all the more considerable the greater the surface. This is seen in the very finely divided platinum which is obtained on reducing alkaline platinum solutions with organic substances, e.g. formic acid (p. 402). The metal is then deposited in the form of a very fine powder which, on account of its black colour, is called *platinum black*, and which exhibits the above-mentioned catalytic properties in a high degree. On being heated to redness, it cakes together, and forms grey spongy platinum.

Besides the catalytic actions, platinum black also exhibits absorption phenomena which, by reason of its fine division and correspondingly large surface, are as clearly seen as in the case of charcoal (p. 389). On account of this property it is somewhat difficult to prepare platinum black pure.

Finally, platinum is obtained in the most finely divided state by disintegration by means of an electric arc under water (Bredig). A black brown coloured colloidal solution is then produced, which exhibits perfectly similar catalytic actions to the other forms, even when present in extremely small amounts. By addition of salts, the platinum is readily precipitated from these solutions, and thereby loses a great part of its catalytic activity.

* Apparently connected with these catalytic actions is the property of platinum of dissolving large quantities of different gases, especially hydrogen. Hydrogen diffuses through red-hot platinum with the greatest ease; but, even at the ordinary temperature, platinum, especially in the form of platinum black or spongy platinum, can absorb fairly large quantities of the gas. The hydrogen thereby increases enormously in reactivity, and acts in accordance with its position in the potential series (in the neighbourhood of lead), reducing, for example, more noble metals from their salts, and forming the corresponding compounds, i.e. the acid. It must not be supposed that the chemical affinity or the chemical potential of the hydrogen is changed; such an assumption, which is certainly very often made, would be a contradiction of the fundamental laws of the theory of energy. For, if it were the case, one might generate hydrogen without the presence of platinum, and then in the presence of platinum allow it to pass again into the same combination, and would use up less work for the first process than is gained in the second; in other words, any amount of work whatever would be obtained without expenditure, or from nothing. This, however, is shown by experience to be impossible.

* The cause of the changed action of the platinum lies rather in the *acceleration* of the reactions of hydrogen, and is, therefore, a catalytic action. Gaseous hydrogen reacts so slowly at the ordinary temperature that it appears like an indifferent substance, and from the fact that in the presence of platinum the reaction becomes visible in a short time, while otherwise it would require hours or perhaps

ears, the view has arisen that there is a change of the chemical potential.

772 **Compounds of Platinum** occur in two series, in which the metal acts as divalent or tetravalent. The latter are the better known and the more stable.

Elementary platinion is formed neither in the one nor the other series in any considerable amount; on the contrary, all the more stable compounds of this metal are of a complex character. The variety of these complexes is exceedingly great; only a very few of them can be treated here.

On dissolving platinum in aqua regia, a yellow-red solution is formed which, on evaporation, yields crystals of *hydroplatinichloric acid*, H_2PtCl_6. This compound is a strong dibasic acid, which does not contain any considerable amount of chloridion, for it does not give a precipitate of silver chloride with silver salts, but one of silver platinichloride, Ag_2PtCl_6. Further, on electrolysing a solution of the acid or one of its salts, it is found that the platinum moves towards the anode and not to the cathode, for the liquid during electrolysis in the neighbourhood of the cathode becomes poorer, and in the neighbourhood of the anode richer in platinum,[1] which shows that the platinum is not present as a cation.

Of the salts of hydroplatinichloric acid, we have already met with the difficultly soluble *potassium salt* (p. 450), since it is used for the separation and analytical estimation of potassium. It is a salt which crystallises in anhydrous, regular octahedra, and is much more readily soluble in hot than in cold water. By addition of alcohol it is almost entirely precipitated from its aqueous solution.

Sodium platinichloride is readily soluble in water, and crystallises with $6H_2O$. *Ammonium platinichloride* resembles the potassium compound in being difficultly soluble; it is used for the separation of platinum from the solutions of the crude platinum ores. On being heated it readily decomposes into ammonium chloride and chlorine, which escape, and metallic platinum, which remains behind in the form of spongy platinum (p. 761).

By carefully heating hydroplatinichloric acid in a current of chlorine, *platinum tetrachloride*, $PtCl_4$, is obtained as a crystalline mass similar to hydroplatinichloric acid, but not deliquescent. It readily dissolves in water; the solution contains, like that of gold chloride, an oxy-acid, H_2PtCl_4O, which is formed by the absorption of the elements of water. The very dilute solutions have the remarkable property that their conductivity very rapidly increases when they are illuminated,

[1] At the electrodes themselves the reaction is apparently the opposite, metallic platinum separating out on the cathode. This is, however, a secondary reaction due to the fact that the hydrogen, which is conducted by the current to the cathode, is not discharged there, but reduces the platinum solution present, and the metal is deposited.

a behaviour which is probably connected with a hydrolysis and splitting off of hydrochloric acid.

On adding excess of sodium carbonate to a solution of hydroplatinic chloric acid, concentrating and extracting the residue with acetic acid, *platinic hydroxide*, $Pt(OH)_4$, is obtained as a red-brown powder, which is soluble in strong acids (but not in weak acids like acetic acid) and in alkalis. The solutions in acids contain platinic salts, which are greatly dissociated hydrolytically, but presumably also contain a little *tetraplatinum* (Pt); they are of a yellow-brown colour. The alkaline solutions contain *platinates*, i.e. salts of the acid H_2PtO_3, some of which have been prepared in the solid state.

From the solutions of the platinum compounds, sulphuretted hydrogen slowly precipitates black *platinum sulphide*, which dissolves in excess of alkali sulphides to a dark-brown solution, with formation of a thioplatinic acid.

From the compounds of platinichloridion, compounds of *platino-chloridion* $PtCl_4''$ are formed by means of reducing agents. Thus, on warming an aqueous paste of potassium platinichloride with cuprous chloride, a dark solution is obtained from which dark-red crystals of the soluble salt K_2PtCl_4 separate out. The free acid is known only in solution; the anion $PtCl_4''$ is ruby-red in colour. The potassium salt is employed in photography for the production of platinotypes, which consist of metallic platinum. For this purpose it is spread on paper, along with ferric oxalate, and exposed to light; in the light the ferric salt is reduced to ferrous salt (p. 592). If the paper is then passed through a solution of potassium oxalate, a reduction of the platinum occurs at those parts at which the action of light had occurred, and a positive is obtained in a grey-black colour which, in accordance with the stability of metallic platinum, is very resistant to air and light. With a very weak acid solution of potassium platino-chloride, also, silver prints can be converted into platinum ones, i.e. one can "tone" with platinum.

From the solutions of the platinochlorides, alkalis precipitate black *platinous hydroxide*, which has no acid properties.

Platinous chloride, $PtCl_2$, is obtained by heating hydroplatinic chloric acid to 250°-300°, or by heating spongy platinum to the same temperature in a current of chlorine. It is a green-brown powder, which does not dissolve in water, but is readily soluble in hydrochloric acid; with the latter it forms a hydroplatinochloric acid.

On passing carbon monoxide over platinous chloride, very remarkable compounds are formed which contain the components in the proportions 1:1, 1:2, and 1:3. The first volatilises without decomposition at about 250°, and thus stands in conspicuous contrast to all other platinum compounds, which are not volatile, but decompose in the heat. They are yellow or yellow-red crystalline substances.

On allowing a solution of potassium platinochloride to stand with potassium nitrite in a warm place, *potassium platinonitrite*, $K_2Pt(NO_2)_4$, crystallises out in colourless, difficultly soluble crystals. The free acid, $H_2Pt(NO_2)_6$, has also been prepared. The salts readily take up six combining weights of halogen.

Of the numerous other series of complex compounds which platinum forms, we may still mention the ammonia and the cyanogen compounds. The *ammonia compounds* belong to two series, corresponding to the platinous and platinic compounds. Their empirical composition is that of divalent or tetravalent salts of platinum combined with one to four combining weights of ammonia, NH_3, often along with water. Moreover, they exhibit specific properties, showing that they are salts of new cations in which neither the ammonia nor the platinum gives its usual reactions. These compounds are very similar to the corresponding compounds of cobalt (p. 623), more especially also in the fact that the halogens and acid residues present are only partially separated as ions, and in part form constituents of the cations. The hydroxides of several of these have been prepared, and are soluble substances with a strongly alkaline reaction. For the theory of these compounds cf. p. 624.

The complex compounds with *cyanogen* are derived from the divalent *platino-cyanidum*, $Pt(CN)_2$. The potassium salt is formed by dissolving platinous chloride in a solution of potassium cyanide, or also by melting potassium cyanide with spongy platinum; it is a bright yellow salt exhibiting a blue iridescence. The barium compound is formed by mixing platinous chloride and barium carbonate in water, and passing hydrocyanic acid into the hot liquid. It is a bright yellow salt exhibiting violet-blue iridescence. The magnesium salt which can be prepared in the same way, is crimson red with a green metallic lustre, the property of surface iridescence, dependent on the crystalline form, being possessed by all the salts of this series. The barium compound also exhibits in a very marked manner the phenomenon of fluorescence, and it converts, not only the ordinary ultra-violet, but also the Röntgen and uranium rays (p. 746) into visible light, and its application is in accordance with this property.

From the solution of the barium salt, the free *hydroplatino-cyanic acid* is obtained by means of dilute sulphuric acid; it is colourless in solution, but in the solid state it exhibits a variety of lustrous colours, according to the amount of water it contains.

The salts of this series readily take up two combining weights of halogen, but these are only feebly united; the corresponding compounds likewise generally crystallise well.

773. Palladium.—Palladium was discovered by Wollaston in 1803 in platinum ore. It is the least noble of the platinum metals, as it readily dissolves in nitric acid. It resembles platinum in its combining

relations, for it forms divalent and tetravalent compounds; in this case, however, the divalent compounds are the more stable.

Metallic palladium has a density of 11·8, and melts at 1500   It is a metal similar to platinum, and has the special property of uniting with large amounts of hydrogen to form a compound of metallic appearance, the nature of which has not yet been sufficiently explained. The combination of the two substances takes place most rapidly at 100 , and is all the more rapid the more finely the metal is divided. With finely divided metal, 800 volumes of hydrogen are absorbed by one volume of the metal.   Still more hydrogen is absorbed in employing the metal as cathode in dilute sulphuric acid; the amount of gas then absorbed increases with the strength of the current a portion of the hydrogen so absorbed, however, escapes immediately the current is stopped, while another portion is in stable combination. If the temperature is raised, the palladium hydride again decomposes into its components; it does not, however, follow the ordinary law of dissociation, according to which the pressure is independent of the degree of decomposition , in this case there is a dependence.

The hydrogen absorbed by palladium has a strongly reducing action, and it has therefore often been regarded as existing in a special condition.   In this case, however, as in the case of platinum, we are dealing only with a catalytic acceleration of the reaction.

* If galvanic cells are constructed containing hydrogen along with various metals, such as gold, platinum, or palladium, no electromotive force is observed if the hydrogen is always present in excess.   This is a proof that the chemical potential of the hydrogen is not increased by the palladium.

Of the chemical compounds of palladium, *palladious nitrate*, $Pd(NO_3)_2$, may be mentioned, which is formed by dissolving the metal in nitric acid.   It is a very deliquescent salt, the solution of which is dark brown in colour; this colour may be ascribed to dipalladion, Pd''.   On adding alkali carbonates to these solutions, carbon dioxide is evolved, and a dark brown precipitate of palladious hydroxide, which on ignition decomposes only with difficulty into metal and oxygen, is deposited.   Dipalladion unites with iodidion to form a dark-brown compound, which is soluble with extreme difficulty in water. Since bromidion and chloridion do not give such a precipitate, palladious nitrate can be used as a reagent for iodidion.

If palladium is dissolved in a large excess of aqua regia, a solution of *hydropalladichloric acid*, H_2PdCl_6, is formed from which the potassium salt can be obtained as a difficultly soluble crystalline powder consisting of scarlet octahedra.   Even on heating the acid solution to boiling, chlorine escapes and *hydropalladochloric acid*, H_2PdCl_4, is formed, the potassium salt of which is very similar to the corresponding platinous compound (p. 764).

On evaporating a solution of palladium in aqua regia to dryness

ydrogen chloride and chlorine escape, and *palladous chloride*, $PdCl_2$, obtained, which dissolves in water with a red-brown colour.

The combining weight of palladium is Pd = 106.5.

774 **Iridium.**—On treating platinum ore with aqua regia, part of the iridium is dissolved along with the platinum, and part remains alloyed with osmium as osmiridium, which is not attacked by aqua regia. The dissolved portion is precipitated along with the platinum by means of ammonium chloride, and its presence is recognised even in comparatively small amounts by the fact that the compound of platinum chloride and ammonium chloride has a yellow red or red-brown colour instead of bright yellow. This portion of iridium is often left in the platinum used in the arts, since the metal thereby becomes harder and more resistant to chemical influences.

Pure iridium scarcely melts even in the oxyhydrogen flame, and can be worked only with difficulty. It has the density 22, the hardness of slightly tempered steel, and is only slowly attacked even by aqua regia; it is more readily attacked when it is in a state of fine division. On gently heating a mixture of the metal and common salt in a current of moist chlorine, the former can be converted into the sodium salt of divalent iridichloridion, $IrCl_6$".

Iridium forms three series of compounds in which it is di-, tri-, and tetravalent. The divalent compounds are the least stable and are little known; the other two series pass very readily one into the other, so that it is hardly possible to say which is the more stable. In both series the typical compounds are the complex iridiumchloride ions—the trivalent iridochloridion, $IrCl_6$''', and the divalent iridichlorid-ion. $IrCl_6$". The former anion is green-brown, the latter dark-red. The change of colour accompanying the ready conversion of the two series into one another gave rise to the name of the element (from *iris*, a rainbow).

Potassium iridichloride, K_2IrCl_6, resembles potassium platinichloride in its solubility relations; it crystallises in small dark red octahedra, and is obtained by heating a mixture of finely divided iridium and potassium chloride in a current of moist chlorine to a gentle red heat. The corresponding sodium salt crystallises like the platinum compound with $6H_2O$, and is readily soluble. By reduction with sulphurous acid in acid (or with alcohol in basic) solution, chlorine and sodium chloride are split off, and sodium iridochloride, $Na_3IrCl_6 \cdot 12H_2O$, which is a very soluble salt, is obtained. The potassium salt obtained in a similar manner from the iridichloride, is also readily soluble. Both are readily reconverted by oxidising agents into the higher series.

With ammonia iridium forms numerous complex bases, which are similar to those of platinum.

The combining weight of iridium is Ir = 193.0.

775. **Rhodium.**—Rhodium stands to iridium in a relation similar

to that of palladium to platinum. Like iridium it forms three series of compounds; in contrast with iridium, however, the highest series is here the least stable. This depression of the region of stability towards the lower type is present also in the case of palladium compared with platinum, and occurs in both cases in the element of lower combining weight.

Rhodium occurs in comparatively small quantity in platinum ores. It was discovered in 1803 by Wollaston, and has obtained its name from the rose-red colour of its salts.

Metallic rhodium is less refractory than iridium, but more so than platinum. In the pure state it is ductile and has the density 12. The finely divided metal has very pronounced catalytic properties; for example, it decomposes formic acid in aqueous solution into hydrogen and carbon dioxide: $H_2CO_2 = H_2 + CO_2$, i.e. it so greatly accelerates this reaction, which takes place of itself in very small amount, that the gases escape with effervescence. Other organic compounds are also changed in a similar manner; this is a proof that very many of these substances are unstable compounds, and gain in appearance of stability only from the slowness of their spontaneous decomposition.

The best known compounds of rhodium are those of the trivalent type; from these, apparently, two different rhodiumchloride ions, viz. $RhCl_6'''$ and $RhCl'''$, appear to be derived; salts, at least, of these two types are known. The alkali salts are soluble with a red colour in water.

A fairly large number of complex ammonia compounds are also known in the case of rhodium.

The combining weight is $Rh = 103.0$.

776. Osmium and **Ruthenium** are distinguished in a very characteristic manner from the other four platinum metals by their property of forming *readily volatile oxygen compounds*; these are produced, although slowly, by heating the metals in the air, and volatilise with the steam in the treatment of the crude platinum ore with aqua regia. These compounds contain four combining weights of oxygen to one of the metal, and behave as almost indifferent substances; at all events, the acid properties of the hydroxides (unknown in the free state) are only feebly developed.

Osmium has the density 22·5 in the crystalline state and is the densest of all known substances. It is almost infusible, is very hard, is insoluble in aqua regia, but passes slowly into the volatile tetroxide on heating in oxygen. By fusion with zinc and treatment of the alloy with hydrochloric acid, it is obtained in a finely divided state as a black powder, which, on being heated in the air, smoulders and forms the tetroxide; from tin, however, it is obtained in crystals with a metallic lustre.

Osmiridium, which remains after treating the platinum ore, forms

hard, silver-white laminæ, and is used for tipping gold pen-nibs, which do not wear down with use.   On being heated with common salt in a current of wet chlorine (*vide supra*) the osmium volatilises in the form of the tetroxide.

Osmium tetroxide is a white, readily fusible crystalline mass which slowly dissolves in water and readily volatilises with steam.   It has a strong, very unpleasant smell, recalling that of chlorine, and a highly poisonous action, because it is reduced by the tissues to metallic osmium, which is deposited and exercises a continual irritation ; the eyes, more especially, are powerfully attacked.   The solutions exhibit oxidising actions but no acid reaction ; if an alkali is added, the greater portion of the tetroxide can then be distilled off, showing that the corresponding salt undergoes hydrolysis to a large extent, and is therefore formed only in very small amount.

Aqueous solutions of osmium tetroxide are used in histology for hardening animal tissues.

On careful reduction, the alkaline solutions of osmium tetroxide are converted into the salts of *osmamion*, OsO_4'', the acid not being known either in the free state or as the anhydride.   That a new anion has been formed is evidenced by the fact that the liquid, which was previously colourless, becomes red violet ; on addition of acids, however, the osmic acid decomposes into tetroxide, which volatilises, and the hydroxide of tetravalent osmium, which is deposited as a black precipitate, if any oxyacid has been used ; in hydrochloric acid, however, the latter is soluble.

With chlorine, osmium forms two osmium-chloride ions, $OsCl_6''$ and $OsCl_6'$.   The former anion is cherry red, the latter golden yellow. The salts of the second series are formed by treating osmium and alkali chlorides with moist chlorine, those of the first are obtained by the reduction of the latter, and are unstable.

Finally, osmium compounds of a divalent type have been obtained by the reduction of the higher compounds.   The corresponding salts, in which the osmium is present as a divalent cation, are dark blue in colour ; they oxidise very readily to a higher stage.

The combining weight is $Os = 191$.

777.   **Ruthenium** was discovered by Claus in 1845.   It is a grey metal of density 11, which fuses only with difficulty but more readily than osmium.   It is fairly resistant to aqua regia ; on fusion with caustic potash and saltpetre it is attacked with formation of potassium ruthenate.

On distilling the solution produced while a current of chlorine is at the same time passed through it, *ruthenium tetroxide* passes over as a yellow crystalline mass, which melts as low as 26°, and boils about 100° ; at this temperature, however, explosions readily occur.   It seems to be formed also in minute traces on heating the metal in the air.   The vapour is yellow, and the molar weight corresponds to the

3 D

formula RuO_4.   It dissolves in water, forming a yellow liquid, which is unstable.

From the oxide, two series of salts are formed with bases, with loss of oxygen, viz. the dark green *perruthenates*, $MRuO_4$, and the orange-red *ruthenates*, M_2RuO_4; between these two, therefore, the same relation exists as between the permanganates and the manganates, and their reciprocal transformation also takes place under perfectly similar conditions, the latter being more stable in alkaline liquids, the former in acid or neutral.

With chlorine, ruthenium forms compounds of the di-, tri-, and tetravalent type; the last two form rutheniumchloride ions, $RuCl_5'$ and $RuCl_6''$; the former are yellow, the latter red.

The combining weight of ruthenium is $Ru = 101 \cdot 7$.

CHAPTER XLIV

378. General.—In the preceding chapters the question as to which of the possible multiples of the combining weight of each element is the most suitable has not been discussed, and we now proceed to examine whether a general answer can be given to the question at all.

As the most obvious rules for the choice of the combining weights, the two following will evidently be laid down, viz. the formulæ shall, in the first place, be as *simple* as possible, and, in the second place, *similar compounds shall have similar formulæ*. These two rules lead, in many cases, to concordant results—in other cases, however, to contradictory ones.

Thus, according to the *principle of simplicity*, the combining weight of those elements which form only one compound with oxygen will be chosen, so that the compound contains *one* combining weight of each element. This is, for instance, the case with zinc and cadmium, whose oxides are written ZnO and CdO. In the second place, in accordance with the *principle of similarity*, of the two oxygen compounds of copper, cupric oxide must be formulated in agreement with zinc oxide, because these two exhibit various points of similarity in their compounds. Hence, it follows, that cuprous oxide must be written Cu_2O.

If now, we are dealing with silver oxide, we should, in accordance with the principle of simplicity, write the formula AgO, and make $Ag = 215.8$. This, however, would be in conflict with the second principle, for the silver compounds are very similar to the cuprous compounds. We have the choice, therefore, of violating the one or other principle: they cannot both be followed at the same time.

Similar holds in the case of iron and aluminium. On account of its similarity to zinc oxide and cupric oxide, ferrous oxide must be written FeO; from this, the formula Fe_2O_3 would follow for ferric oxide. Aluminium forms only one oxygen compound, and would, therefore, in accordance with the principle of simplicity, have to be written AlO, Al being made equal to 40.5. In this way, however, attention is not paid to the undoubtedly very great similarity to ferric

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oxide, and in order to give expression to this we must write Al_2O_3, and thus violate the principle of simplicity.

To give effect to both of the above principles at one and the same time is not possible without producing contradictions, and one has often to decide which of the two principles one will violate. In general, the principle of similarity has the preference.

779. Isomorphism.—It is, however, not easy in any given case to decide as to the degree of similarity to be taken into account. Silver oxide and lead oxide also show a considerable amount of similarity in their general relations, more especially in respect of the solubility of their salts, and yet the two are differently formulated, viz. Ag_2O and PbO. In order to arrive at definite rules, we must give up the general "similarity" and choose some demonstrable property as basis. In *isomorphism* (p. 311) we obtain such a property. We shall therefore lay down the principle : The combining weights shall be chosen such that isomorphous substances have similar formulæ. As a matter of fact, this principle can be followed without obtaining contradictions, and all isomorphous pairs and groups mentioned in this book have received concordant formulæ.

A complete system of combining weights, however, cannot be obtained in this way, since the isomorphous groups are mostly restricted to a small number of compounds, and the relations existing between elements belonging to different groups (*e.g.* manganese) are not sufficient to unite all the groups. Further aids must therefore be looked for.

780. The Molar Weight.—Such an aid is afforded by the conception of molar or molecular weight, if we lay down the condition that *all formulæ corresponding to a molar weight shall contain only a whole number of combining weights of the elements* (p. 90). The molar weight is a number which can be deduced from the gaseous density or from the depression of the freezing point or elevation of the boiling point (p. 159), and which can be determined independently of doubtful suppositions, and purely by experiment. The question whether the above condition is fulfilled can therefore be tested in the case of all substances which can be observed in the gaseous state or of which solutions can be prepared. As a matter of fact, various doubtful cases have been decided by this means. Thus, for example, beryllium was regarded by many investigators as an earth metal, and its chloride was, in analogy to that of aluminium, written $BeCl_3$, *i.e.* there was taken as the combining weight of beryllium that weight which was combined with 3×35.46 parts of chlorine, viz. 13.5. When, however, one succeeded in determining the vapour density of beryllium chloride, its molar weight was found to be 80. From this it follows that only *two* combining weights of chlorine can be contained in beryllium chloride. The combining weight of the element must therefore be taken as 9, and the chloride be written $BeCl_2$.

hese considerations, of course, lead much further than those of
rphism alone, but even they are not perfectly decisive.   It is,
d, conceivable, although generally not very probable, that besides
ompounds whose molar weights are known, other compounds of
ticular element exist, the molar weight of which contains only a
on of the combining weight deduced from the former compound.
would not necessitate a contradiction to the other compounds, but
l merely lead to the assumption of several combining weights in
rmer compounds.   In other words, from the molar weights there
e deduced only the limit above which the combining weight does
ie, but it cannot be proved that the combining weight is not
tion of that hitherto chosen.

81. **The Atomic Heat.**—A law discovered in 1818 by Dulong
Petit, and which has since then been confirmed in many other
, admits of no such doubt.   This states that the thermal capacity
e elements referred to one combining weight, or the *atomic heat*,
stant and equal to about 6 calories or 25 *kj* for each degree.

By the term thermal capacity of a body there is understood the
between the amount of heat communicated to the body and the
tion of temperature which the latter experiences.   If, therefore,
heat Q is introduced into the body, the temperature of which
by rises t, the thermal capacity of the body is $k = Q/t$.   This
ity k is evidently proportional to the weight of the body investi-
, for the elevation of temperature will be smaller in the same
rtion as the amount of substance increases to which the same
ity of heat is communicated.   It has, however, also been found
equal weights of different substances experience very different
tion of temperature with the same amount of heat, that is,
her words, the specific heat of different substances is different,
he term *specific heat* has been applied to the thermal capacity
ed to the unit of weight.   If, however, we refer the thermal
ity not to equal weights, but weights which are in the ratio
e combining weights, *these quantities of substance have the same
al capacity* when we are dealing with the *elements* in the solid
.   Calling the thermal capacity referred to the combining or
ic weight, by the name *atomic heat*, the law states that *the atomic
of the solid elements are equal.*

This law is not universally valid.   In the first place, as above-
ioned, it is valid only for the solid state, liquid, and especially
us elements, are not subject to it.   Further, it is valid not for all
elements, but only for those whose combining weight is not less
30.   The elements which are below this limit have, in the sense
e law, too small an atomic heat.

82. **Result.**—If we now ask how these different principles for
hoice of the combining weight can be united, in so far as they
the same elements, we find that they agree well with one another.

A system of combining weights can be drawn up which allows of the expression of all isomorphism relations by concordant formulæ, and of all molar weights by integral values of the combining weights, and whereby also the atomic heats of the solid elements (with combining weight above 30) are expressed by approximately the same numbers. These are the combining weights of which use has been continually been made in this book, and which are at the present day universally accepted by the chemists of all countries. Nowhere in this work has it been necessary to write formulæ representing actually determined molar weights with fractions [1] of the combining weights. Further in all cases of isomorphism, the formulæ of isomorphic compounds are similar, and that the rule of Dulong and Petit is fulfilled is seen from the following table :—

Element	A_v	Element	
Lithium	28	Molybdenum	29
Beryllium	16	Ruthenium	26
Boron	15 to 17	Rhodium	2
Carbon	3 to 24	Palladium	27
Sodium	28	Silver	29
Magnesium	26	Cadmium	23
Aluminium	24	Indium	27
Silicon	16 to 24	Tin	27
Phosphorus	23	Antimony	26
Sulphur	24	Tellurium	27
Potassium	27	Iodine	8
Calcium	28	Lanthanum	20
Chromium	26	Tungsten	29
Manganese	28	Iridium	27
Iron	26	Platinum	27
Cobalt	26	Gold	26
Nickel	27	Osmium	29
Copper	25	Mercury	27
Zinc	23	Thallium	28
Gallium	23	Lead	27
Arsenic	26	Bismuth	26
Selenium	25	Thorium	27
Zirconium	26	Uranium	28

783 The Periodic System.—Attention has been repeatedly drawn to the existence of regularities between the combining weights of similar elements, which generally assumed the form that the differences in the numerical values of corresponding elements in different groups are approximately equal. The question here arises whether we are dealing with any fairly general regularity, and if so how this is to be expressed

The answer has been sought for in very different ways. As usual, the simplest has been arrived at last. If the elements are arranged in a series simply according to the numerical values of the combining

[1] In some few cases fractions have been written in the statement of the water of crystallisation of salts. Since at present molar weights can be determined only in gases or vapours and for dissolved substances, but not for solid substances, no such limitation exists.

weights without regard to any other circumstance, the following is the result.

In this series similar elements always occur at regular intervals. If then the series is divided into a number of sections, so that each section commences with a member of a definite family, it is found that the second, third, and following positions of the sections are also filled by elements corresponding to one another.

The table on p. 776 has arisen by dividing the series of the elements, as determined by the values of the combining weights, into such sections; these sections have then been placed one below the other. In this way perpendicular columns are obtained in which similar or related elements stand under one another.

The different rows have also been alternately shifted somewhat relatively to one another. As can be seen, the mutual relation between those elements which are most closely allied to one another thereby receives better expression.

Thus, in the column headed 0, we find all the elements of the *argon type*, which are distinguished by their inability to form chemical compounds. Under I. there are, on the one hand, the monovalent alkali metals, on the other hand the *monovalent* heavy metals, copper, silver, gold.

Under II. there stand the *divalent* alkaline earth metals, and along with them the *divalent* heavy metals of the zinc group.

Under III. are the *trivalent* earth metals along with the corresponding heavy metals, gallium and indium.

Under IV. the *tetravalent* elements are found. The first representatives of these have no longer a metallic character, just as the first non-metal appeared in the preceding group in the case of boron; the metals of the titanium group on the one hand, and of the tin group on the other, then follow.

Column V. also contains, to begin with, non-metals which can act as *trivalent* or as *pentavalent*; in the lower portion there are the corresponding tri- and pentavalent metals.

In column VI. are *di-* and *hexavalent* elements; the non-metallic character can be followed further down the column.

Column VII. contains the typical non-metals, the halogens, which can act, on the one hand, as *monovalent*—on the other hand, as *heptavalent*.

Finally, the last column contains the two families of the iron metals and the platinum metals, which do not quite fall into line with the rest of the system.

In all these columns the general rule can be observed that the basic properties (i.e. the tendency to form cations) increases with increasing combining weight; the power of forming anions, however, decreases.

As can be seen, the table is not complete, but contains many positions *unfilled*. It cannot be otherwise, for there is no justification for the assumption that all existing elements have already been dis-

PERIODIC ARRANGEMENT OF THE ELEMENTS

0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
He, 4								
	Li, 7	Be, 9·1	B, 11	C, 12	N, 14	O, 16	F, 19	
Ne, 20								
	Na, 23	Mg, 24·4	Al, 27·1	Si, 28·4	P, 31·0	S, 32·1	Cl, 35·5	
A, 39·9	K, 39·1	Ca, 40·1	Sc, 44·1	Ti, 48·1	V, 51·2	Cr, 52·1	Mn, 55·0	Fe, 55·9 Ni, 58·7 Co, 59
	Cu, 63·6	Zn, 65·4	Ga, 70	Ge, 72·5	As, 75	Se, 79·2	Br, 80	
Kr, 81·8	Rb, 85·4	Sr, 87·6	Y, 89	Zr, 90·6	Nb, 94	Mo, 96·0	…	Ru, 101·7 Rh, 103 Pd, 106·5
	Ag, 107·9	Cd, 112·4	In, 114	Sn, 119	Sb, 120·2	Te, 127·6	I, 126·8	
X, 128	Cs, 133	Ba, 137·4	La, 138·9, etc.	…	…	…	…	
			Yb, 173	…	Ta, 183	W, 184	…	Os, 191 Ir, 193 Pt, 194·8
	Au, 197·2	Hg, 200	Tl, 204·1	Pb, 206·9	Bi, 208·5	…	…	
…		Ra, 225		Th, 232·5		U, 238·5		

covered and investigated. It is, however, worthy of notice that up to the combining weight 140, scarcely an element is wanting   At this point there is a large blank, and only between 170 and 240 is there again some degree of completeness.   At the time, about 1860, when the regularities above described were discovered by Newlands, L. Meyer, and Mendeleef, many more of the elements were wanting, and it was possible, according to the law of similarity, to predict with very fair approximation the properties of those elements whose places were empty.   In this way Mendeléef, especially, predicted the properties of several elements unknown at that time, and the discoveries which were subsequently made amply confirmed most of these predictions.

Besides the general relations of chemical combination, the arrangement of the elements according to the magnitude of their combining weights affords a fairly complete *systematisation of the physical properties*, both of the free elements and of their corresponding compounds.   Thus, on passing continuously along the horizontal rows, we pass through a regular transition from the region of the metals to that of the non-metals, to again commence with metals at the beginning of a new row.

The whole series, then, falls into a number of periods, and the whole system has therefore received the name *periodic law*.   The periodic character is seen most clearly by graphically representing definite properties of the elements.   Such a representation is given in Fig. 126 of two properties, the atomic volume [1] and the melting point.

Most of the properties of the elements, so far as they can be measured, yield similar figures, so that it has been stated generally *The properties of the elements are periodic functions of their combining weights*.

The same relations are seen also in the case of comparable compounds, *e.g.* the oxides, chlorides, sulphides, etc., in respect of their different properties.   Compare, for example, the solubility relations of the chlorides of the elements and their behaviour generally with water, in the light of the table.

The form of the above regularities, finally, leads to the view that the values of the combining weights themselves must stand in a regular relation to one another.   The first idea is that the members are characterised by constant differences of their combining weights. We can at once satisfy ourselves, however, that only a very rough approximation to such a relation exists.   Thus, for example, the differences between the corresponding elements of the first and second horizontal series amount to—16, 16, 15·3, 16·1, 16·4, 17·0, 16·1, 16·5, and is therefore fairly constant although the deviations are far above

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[1] By atomic volume is meant the product of the extensity and the combining w In accordance with the definition of extensity (p. 27) it represents the volume occupied by the combining weight in grams of the particular element

THE END